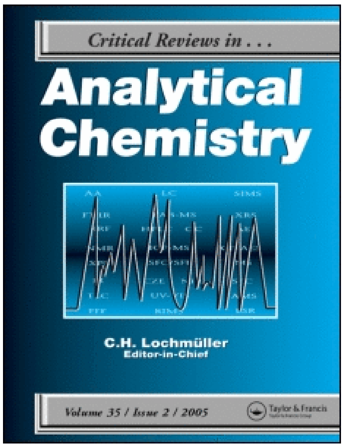

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METROLOGICAL ASPECTS OF QUANTITATIVE ANALYSIS

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I. INTRODUCTION

A. Scope and Purpose of Review

This review is devoted to the problem of correspondence between the results of quantitative analysis and the real contents of the components being determined in the sample (or in a mass of substance of similar purpose if the analysis is made without sampling). It is a problem of precision and accuracy, or, in general, of the reliability of the analytical results. It is possible that after reading this preamble a certain number of readers will think that we are going to discuss statistical formulas, and may, therefore, lose further interest. We appeal to the reader to have patience: the problem is much wider.

Every critically inclined analyst, especially the head of an analytical laboratory, is preoccupied with the question: do the analytical result errors lie within the tolerable limits? If the answer is positive, the subsequent questions arise: how full is the guarantee that the situation will not deteriorate?; what measures are needed as safeguards? If the answer is negative, one is urged to ascertain how well grounded the requirements are in respect to limitation of errors. If such requirements are objective, it is necessary to decide what must be done to reduce the errors in the obtained results to acceptable levels and ensure that they remain at these levels. Administrators of higher rank and research workers engaged in the general problems of the analytical service in industry, farming, health care, protection of the environment, as well as in scientific research, come to the conclusion that it is necessary to work out a certain general approach for the most efficient solution of the problem of the quality of analytical results based on the criterion of their adequacy in regard to actual content of components.

With the above in view it seemed worthwhile to consider the following aspects: the essence of the concept of reliability as applied to quantitative analysis; real values of errors of the results of determination of various groups of substances; the correspondence of these values to the stipulated requirements; the traditional approaches and means for assuring reliability, their possibilities and limitations; ideas and approaches suggested for the further improvement of the analytical service in regard to reliability of analytical results and experience gained in the course of their implementation; and immediate tasks.

Certain aspects of this problem have been considered in books,[1-8] review and program-setting articles,[9-33] and special publications (see below). We do not consider here some important adjacent fields, e.g., application of methods of mathematical statistics, including those intended for operational monitoring of the quality of analysis[34-38] and chemometrics.[39]

References to publications pertaining to one and the same subject are listed in this review in chronological order. In certain cases references are given to original works, even if they have been published relatively long ago. Taking into account linguistic difficulties of a certain part of the readers and that many papers in Russian have been published in journals of not so much chemical, but rather metrological profile which are not always included in the scope of abstract journals devoted to quantitative analysis, the relevant publications are reviewed in greater detail.

It has not been found possible to give references to all the publications pertaining to the considered problem. Reference has been given to those publications which expound ideas of methodological and practical importance, approaches to and ways of their implementation. Some publications have been mentioned because they provide confirmation of one or other thesis. It is possible, in view of the information explosion, that the reviewer has missed some essentially important publications. The reviewer is ready to offer his apologies to the authors.

B. Initial Points

As is known, all the methods of quantitative analysis (laboratory and the so-called instrument ones), despite their diversity, are based on the common principle of the dependence of the numerical characteristic of some property (precipitate mass, absorption or emission of light, heat conductivity of gas, etc.) on the content of the component being determined. However, in most cases, the measurements of such characteristics cannot be carried out directly. It is necessary to preliminarily create conditions which will allow the analyst to carry out the conclusive measurement and eliminate factors distorting its results. Thus, even in the case of a relatively simple analysis, e.g., the determination of silicon content in electrical steel by the gravimetric method, it is necessary to separate silicon in the form of a silicate precipitate (i.e., create conditions which will allow the measurement of the precipitate mass) and ensure that the precipitate is dry and not contaminated with the oxides of other elements (i.e., exclude causes of distortion of the results).

From the above premise important inferences can be drawn.[2,3,5,11,13,15,40] First, without attempting to belittle the importance and main role of the means employed for the determination of the chemical composition, we must concede that the goal is the acquisition of quantitative data (the result must give the answer to the question of how much of the component being determined is there in the specimen), that is, quantitative analysis is, according to its general aim, a process of measurement of content. Second, the analysis of substances is a complex measurement process which cannot be reduced to a set of metrological operations of weighing, measurement of capacity, intensity of light, etc., but has its qualitative special features: peculiar and complex techniques of bringing the measured object to conditions which will allow us to carry out direct measurements of the quantity which is of interest to us; distinctive techniques of eliminating causes which might lead to distortion of the results; and substantial errors. Very often, especially when physicochemical and physical methods are used, an important feature of the analytical procedure is the preliminary calibration; the establishment of the type of relationship between the content of the component and the numerical characteristic of the "analytical" property (plotting of calibration curves), which can also become a specific source of errors.

All these reasons rightfully necessitate a metrological approach to the problem of quantitative analysis. Such an approach, besides fundamental considerations, is dictated also by the parameters characterizing analysis as a means of investigation and control, the appropriate accuracy is not something which is implied. Moreover, this parameter is more often the most difficult to attain because of the unfavorable features of determination of the composition, complication of analytical tasks, and constantly growing requirements in respect to reliability of analysis results.

C. Brief Historic Note

The application of the metrological approach to the analysis of substances has been delayed with respect to the solution of purely analytical problems. For a comparatively long period of time the liaison between analysis and metrology was only in the application of means of measurement of mass, volume, intensity of emission and absorption of light, and other properties, and also in the use of data on atomic mass and values of associated quantities. Today there still exists the conviction that if the analysis is carried out strictly in accordance with the directions, the result is guaranteed to be reliable. As a consequence, in many standards and directions for analysis the means for monitoring the most substantial errors are not provided; usually with such an approach there is either nothing said of errors, or just a mention is made on the permissible discrepancies between the results of parallel determinations. For justice's sake it should be admitted that even among metrologists there persists the opinion that physicochemical measurements should be regarded as such, while chemical composition is determined, and not measured, hence let the analysts do their business without worrying the metrologists.

Gradually the situation goes on improving in general, although it is not free from growing pains. The latter are in many ways conditioned by traditions prevalent among analysts and metrologists; the analysts regard with distrust the intrusion of unusual concepts into the sphere of chemical reactions and analytical instruments which is dear to their hearts, while metrologists are unaware of the peculiarities of quantitative analysis as a measuring process. In such a situation it is important to consider the problem objectively without being carried away easily by one or the other side. In particular it is important to distinguish several aspects: the correlation between analytical chemistry as a scientific discipline and analytical service as a sphere of implementation of the achievements of the former;[18,19,26,27,31,41] the connection between analytical chemistry and theoretical metrology and, as a consequence, their mutual enrichment;[10,11,15,17,20,42,43] and the connection between the activities of analytical service and applied metrology and, as a consequence, the enhancement of the efficiency of these activities (it is to the latter aspect that most of this review is devoted).

If we are to speak of the development of individual branches in a field wherein analytical chemistry, analytical service, and metrology are in close cooperation, we should mention the development and application of reference materials (RMs). However, if we are to observe logical sequence, the utmost important factor is the development and improvement of analytical methods and instruments: before checking a clock, one must have a clock, and a good one. Although this branch is mentioned here as a very important one, lying at the base of all the others, we shall consider it hereunder only as far as its meterological aspects are concerned.

In regard to RMs, the first investigations in this field go back to the turn of the century. It should be noted that associated proposals and attempts to implement them can apparently be traced to 1870, as evidenced by old publications in Sweden, Germany, the U.S., and Russia. The history of RMs is an interesting subject by itself and it would be a fine idea to produce a collective historic review on the theme with the participation of authors from various countries. Speaking about the modern state of RMs, we note the creation and development of services aimed at satisfying the demand for reference materials and ensuring their most effective employment. This activity has been livened up at all levels from industrial laboratories to international organizations.

Among the other established branches of essentially metrological investigation one should note the development of the theory and practice of miscellaneous methods of monitoring the accuracy of analytical results, except RMs (e.g., reference methods, standard additions method, use of a network of authoritative monitoring laboratories) and diffusion of interlaboratory experiments, and wider application of mathematical statistics to problems of quantitative analysis, including those intended for monitoring purposes.

In the early 1950s the concept was introduced that quantitative analysis is not just a set of purely analytical and measurement operations, but, in regard to its general aim, a measuring process as a whole. The acceptance of this concept as fundamental has led to the necessity of formulating and discussing the more important inferences logically ensuing. One of such inferences is the idea of the feasibility of a general metrological approach based on the use of the so-called verification schemes, i.e., methods of transferring the dimension (value) of a quantity from some definitive means to the level where ordinary (field) measurements are carried out. Another inference is the use of such organizational and methodical techniques practiced in metrological organizations as the certification of measurement methods and accreditation measurement laboratories. Finally, since the end of the 1960s an increasing attention has been paid to the optimization of the activities of the analytical service and other systems connected with it (standardization, quality control, etc.) on the basis of systems approach, including as one of the most important the metrological aspect.

The stages of development of these branches and corresponding publications are considered in more detail, taking into account the scope and aim of this review, in the subsequent chapters.

It should be noted that in the general case it is necessary to ensure not only the correspondence of the analytical result to the content of the component being determined in the specimen (in case of analysis without sampling, e.g., in a flow-line — to the content of substance in the dose forming the analytical signal), but also its correspondence to the mean content in the main mass of the monitored substance. This important problem requires special attention.

D. Concept of Reliability

The recommendations of IUPAC and other authoritative organizations dealing with the presentation of chemical analysis results establish the principle of reliability of results — as a general concept and particular notions: accuracy and precision. According to these recommendations accuracy pertains to the difference between the result (or the mean value) and the true value, while precision pertains to the deviations of the random quantities, that is, to the "scatter" of values.

Considering the purpose of this review, we would like to indicate that the values of quantities characterizing precision and accuracy, and consequently reliability, can vary in time and space (laboratories, analysts, methods). In addition, a superposition of such variations can occur. There is also the possibility of the biasing of all the results of the determination of a component in some substance (group of substances) relative to the true content — such cases occur, for instance, in clinical-chemical analyses when the use of various methods leads to the content "opening up" with different degrees of completeness. Finally, the values of quantities which characterize accuracy have to be estimated against a background of variations of other quantities.

If we look at the essence of the problem more broadly, we have to distinguish four types of reliability[2,7,12] (in particular cases, accuracies). In order to establish these distinctions, it is convenient to consider the process of introduction of some substance (material) into the sphere of interests of society as comprising several stages.

At the first stage, those substances selected from the mass of data on properties (useful and harmful) of substances can be of interest to industry, farming, health services, protection of the environment, and other spheres of activity. After an additional study of these substances, their composition is defined more exactly. With the latter in view it is possible to establish the desirable reliability of the results of analyses which are to be made for the subsequent monitoring of such substances. It is proposed to term this type of reliability as *predictable* reliability. Very often the next stage is the standardization of the composition of the substances (materials) following which certain fixed intervals of the content of components are set ("not more than...", "not less than...", "within...to..."). From the point of view of an analyst the positions of these intervals on the axis of content, the widths of intervals (if they are set as "within...to..."), and the number of decimal places to which their limits are specified (for example: "within 17.0 to 19.0%" or "within 17.00 to 19.00%") have a great significance on which depends the tolerable values of errors of the results of analyses which are to be made. If we are to consider such arguments with respect to one or the other component in one or the other substance (material), we can distinguish another type of reliability — *requisite* reliability of analytical results, that is, a reliability the parameters of which are conditioned by the special requirements of the content norms.

In greater or lesser coordination with the standardization of the content of substances (materials), analytical methods are developed, improved and, finally, standardized. With a properly organized analytical service, the documents dealing with methods of analysis (standards, instructions, etc.) shall contain norms regulating the errors in results. It is proposed to designate the reliability characterized by such norms as *standardized* (normalized) reliability.

Finally, it is obvious that there exists yet another type of reliability — that which is *actually assured* under these or other specific conditions of carrying out analyses.

If we are to view the process as a whole, an optimum state may be said to be one in which the parameters characterizing all the mentioned types of reliability are sufficiently close. Unfortunately, such a situation is not always realized.[2,7-12] From the point of view of analysts and considering their responsibility, it is important to have a correspondence between the requirements stipulated and the reliability of analyses practically realized. However, in the general case, the situation wherein there is no correspondence between requirements and possibilities may be improved not only by perfection of methods and instrumentation, and enhancement of reliability control, but also by a critical evaluation of the validity of requirements. Methodological experience has been accumulated[2,7,12,44-47] in the approach to the reconciliation of requirements and opportunities.

An effective organizational form has been found for this purpose: metrological expertise of the drafts of standards for substances (materials) and methods of analysis thereof[2,7,48,49] with the view of ensuring maximum correspondence in each pair of conjugated norms — the content of given component and the errors in the results of relevant analyses.

Of course, it is possible to use a classification based on other parameters: reliability of the results of field (mass) analyses; of those made for monitoring or arbitration purposes; or for the certification of RMs. The point of each such parameter is clear enough.

II. ACTUALLY ASSURED RELIABILITY OF QUANTITATIVE ANALYSIS RESULTS

A. Fields of Application of Data on Actually Assured Reliability

Practically any type of activity in fields where results of analyses are used, as well as in the analytical service itself and in systems ensuring its functioning, requires that the reliability of analytical results, preferably critically evaluated and generalized, be known and taken into consideration. (Here we draw the attention of the reader for the last time to the fact that both accuracy and precision may be implied in particular cases).

A summary of the fields of application of data on the actually assured reliability of analysis results is presented by Shaevich.[7]

With respect to systems, which are serviced by analysts, it has been noted many times that it is important to reckon the actual errors of analysis made for the purpose of controlling technological processes, standardizing materials, protecting the environment, and maintaining the health service.

With respect to the analytical service activity such data may be used for:

1. Drawing conclusions on the quality of performance of the analyst (instrument), group of analysts (instruments), or laboratory (group of laboratories)
2. Working out directions and programs for the development and improvement of the theoretical foundations and specific methods of analysis which take into account the necessity to concentrate efforts on the strengthening of weak (as regards reliability) links in the analytical service
3. Comparison of the merits of newly developed methods (or their variants) with those known earlier

In application to the activity of systems assuring the functioning of the analytical service such data may be used for:

1. Elaboration of directions and programs for the development and improvement of analytical instruments. Account should be taken of the necessity of concentrating (as in the case of methods) on the strengthening of weak (as regards reliability) links

2. Development of new types of analytical instruments, comparison of the merits of newly developed and instruments in current use
3. Standardization of analytical methods
4. Planning the development of RMs, reference methods, and reference analytical instruments. Account should be taken of the necessity of providing for those sections of the analytical service where the rift between requirements in regard to reliability and the actual level of reliability leads to especially harmful consequences
5. Planning of the metrological characteristics of RMs and means, reference methods, and instruments of analogous application. Their errors should not exceed a certain fraction of the actual errors of field analyses (or reduced values expected after the introduction of such means)
6. Design of analytical laboratories and other facilities of analytical control

Taking into view all the above considerations, it is noted[7] that the acquisition of data on the actual values of errors in the analytical results (grouped according to substances and methods), their critical assessments, generalization, comparison, and application should be regarded as an important part of the job of improving the performance of not only the analytical service itself, but also of the systems to which it caters and the systems which cater to it.

B. Methodical Features of Assessment

1. General Remarks

The acquisition of objective data on the actually assured reliability under extremely varied conditions is a difficult job. Such a job and associated difficulties are not peculiar to chemical analysis,[3,9,50-61] but in this case the full value solution is especially difficult to achieve, since the number of sources of uncertainties is substantially higher while their detection, elimination, or assessment of their action are particularly difficult. Taking this into consideration when discussing the problem of reliability (or more often of accuracy) of the results of analysis, one should bear in mind that it is necesary to use not only concepts, methods, and means of metrology and mathematical statistics, but also the logical professional approach, including a selection of an adequate initial model (metrologists and statisticians of high qualification do not reject this). Unfortunately, the methodology of such an approach has been developed to a substantially lesser extent than that of application of the concepts and methods of mathematical statistics or, for example, of mathematical modeling. Of course, specialists in statistics, data analysis, mathematical modeling, and systems approach note this shortcoming. However, they also assert the impossibility of formulating a sequence of sufficiently concrete actions for performing logical professional analysis of every qualitatively specific situation, limiting themselves to directions on the expediency of reading relevant literature, inviting specialists who are nonmathematicians, etc. In view of this, it is difficult to overestimate the role of qualified experts in the discussion of the reliability problem. In the considered case an ideal team consists of an analyst, statistician-metrologist (or data analysis expert), and a representative of that system which is or will be catered to by the corresponding section of the analytical service (e.g., technologist, clinician, etc.).

It should be noted that sometimes two problems are not distinguished sufficiently; one — the study of causes of errors in analyses and the possibilities of one or the other method in regard to the reliability of results (especially in "expert hands"), the other — an assessment of the level of reliability, actually ensured under certain conditions, e.g., in mass production monitoring.

The object of examination in this review is the second of the two indicated problems, the first problem has been treated.[1,5,8]

For the solution of such problems, as applied to a group of laboratories, use is made most often of the interlaboratory experiment. Strictly speaking, its value lies in that it provides useful information for the solution of the problem in the "direct" approach; if substantial differences in the mean results (of various laboratories or obtained by various methods, etc.) are established actually, this testifies to a low level of actual reliability (or more often, accuracy) or, as metrologists have it, there is insufficient or no compatibility of measurements. However, if there are no grounds to strongly trust the data from one of the laboratories, then it is uncertain which mutually differing results are closer to the true value. Also, it is not always clear whether the general mean (for example, based on the data of all or the majority of participants of the collective experiment) or the median is the closest to the true content (the least biased estimate, as statisticians term it). Cases are known when the result of some laboratory, not coinciding with the general mean or the median, was found to be the closest to the true content. In the "converse" variant with a practically satisfactory (small) difference between the compared data, a possibility exists of the overall error of all the data, i.e., the issue of accuracy remains open. Such situations did occur.

It is methodically more effective to generalize data acquired in the course of the application of RMs and means of similar end-use. However, in this case too, erroneous conclusions are possible, for example, due to incomplete mutual correspondence between RMs and test samples as objects of analysis. Unfortunately, there are very few published data thus generalized and critically assessed. There are also few sufficiently representative data based on the comparison of results of field analyses of the main groups of substances with those obtained under special conditions (in very qualified analytical laboratories, on reference setups, etc.).

In such a situation, in order to work out generalized conclusions on the level of actual reliability, we have to use data of interlaboratory experiments (of course, taking into account their possibilities and limitations).

2. *Special Features of Assessment Based on Interlaboratory Experiment Data*

Besides the limitations of the interlaboratory experiment examined above we have to consider a number of other circumstances important for its planning and interpretation of the results.

Initial data used for the assessment of actual errors in the analytical results in conjunction with probability concepts must satisfy the following requirements:

1. Random quantities should be independent — in the content of the probability theory (a random quantity, as is known, is any variable quantity, the various values of which have definite probabilities of occurrence; if a distribution series of a random quantity X_1 remains invariable for all the values of another quantity X_2, then quantity X_1 is said to be independent of X_2).
2. The accepted model of the investigated general statistical set (e.g., normality of distribution) must correspond to reality.
3. To judge the presence and magnitude of systematic errors and their behavior (relatively constant, variable) one must have the opportunity of comparing the estimates of results with the content determined with sufficient approximation relative to the true value.
4. Data must be representative and typical.

It has been shown[2,7,16,62] that in practice these conditions are realized incompletely because of the following reasons.

The statistical randomness of the analytical results is very often distorted by the rejection of a part of the information: the analyst examines the obtained results critically and may introduce corrections which he deems necessary (exclude doubtful results, repeat the analysis, etc.). This approach is revealed in a still greater degree if, for example, a comparison is to be made with results obtained in another place. Before issuing the official result the analyst examines it thoroughly, compares the data obtained by various analysts, repeats an analysis in doubtful cases, etc. Sometimes the statistical independence of results is distorted if data of the previous analysis of the same specimen or parameters at intermediate stages are known to the analyst. This is sometimes observed in the execution of several parallel analyses, for example.

Some difficulties are encountered in the establishment of a model of the general statistical set. Experience shows that the normal (Gaussian) distribution of the analytical results is not always realized.[2,7,63-65] Moreover, noneliminated, relatively large, common to one or several series of determinations, errors which yield asymmetric distributions, distributions where two or three maxima are encountered, etc. In such cases, as is known, we either have to supply a relatively large amount of additional information for a substantiated establishment of the law of distribution of such errors, or to obtain estimates by means of nonparametric methods.

To fulfill the third condition it is necessary, strictly speaking, to have substances which are measures of content of components. Such substances, unfortunately, are not always available. In these cases we have to choose, as a guideline, for lack of anything better, the mean content of the component, established by using data of an authoritative laboratory or of several laboratories — participants of a collective check (less often to choose the median). Limitations of such an approach have been examined above.

The representativeness of data is achieved by suitable sampling size. However, besides representativeness, we must also ensure typicalness. Thus, if only the best (worst) laboratories of a branch of industry have been subjected to a check, the obtained data may be representative, i.e., they may reflect to a sufficient degree the situation in the laboratories undergoing the check. But it would be unwise to extend the estimate of the situation to all the laboratories of this branch of industry; for this purpose it is necessary to include in the sampling such laboratories which ensure typicalness of results. With a small number of laboratories it might seem worthwhile to make a check of all of them.

With this in view, it has been noted[2,7,62] that the estimates of analytical errors which can be calculated through the use of data from laboratory archives or interlaboratory experiments, are usually too low. In general, they must be regarded as approximate values not only in the mathematical/statistical sense, but also in regard to the "professional" essence of the problem.

As experience shows, if the sources of gross errors are eliminated, then with all the conditions being equal (method, laboratory, group of laboratories), the relative magnitude of errors (in percent of the content) depends largely on the content of the component being determined. It is no mere chance that tolerable discrepancies (which are most often experimental norms) in all the standards for methods of analysis are correlated with the content of the component being determined. Hence, when estimating actual errors it is worthwhile first of all to seek and compare data, characterizing such relationships. With this in view it is usual to estimate and discuss the relationships in the case of two most important situations characterizing: (1) the performance of the "primary cell" — determinations made during a comparatively short period of time by one analyst (instrument) analyzing a given substance by one or the other method; (2) the performance of the laboratory — an organizationally distinct section of the analytical service — under the same conditions.

In the first case it is usual to speak about intralaboratory errors, in the second, about interlaboratory errors. More adequate terms have been suggested,[66] although they have not become widespread: "internal" and "external" estimate of errors.

3. Presentation of Results

The ultimate aim of this section is the generalization and examination of data characterizing the assured reliability of results of analyses in several fields of activity of the analytical service.

These data are presented mainly in the form of graphs linking the estimates of values of the quantities $s_{r,1}$ or $s_{r,2}$ and content C. Here $s_{r,1}$ is the relative standard deviation pertaining to the sets of intralaboratory data, $s_{r,2}$ is the same, pertaining to the sets of interlaboratory data. The use of relative quantities is preferable since it gives the opportunity of estimating what part of the measured quantity is constituted, for example, by the error limit (with a certain confidence probability). Besides, for most physical and many physicochemical methods of analysis the use of such parameters is traditional.

The values of $s_{r,1}$ and $s_{r,2}$ are henceforth expressed in percent (of content).

Considering the approximate nature of such relationships and that the mean estimates of contents do not differ substantially from their true values C, the latter are laid off on the X-axis.

The general regularity of such relationships is the growth of the relative error with the decrease of the content being determined. For a wide interval of contents this regularity can be approximated by some function.[2-4,62,67,68] It is accepted usually that

$$s_r = s_r^o C^k \tag{1}$$

where s_r^o is the value of s_r for $C = 1\%$; $0 < k < 1$. After taking the logarithm of $s_{r,1}$ and $s_{r,2}$ we have

$$\lg s_{r,1} = - p \lg C + \lg s_{r,1}^o \tag{2}$$

$$\lg s_{r,2} = - p \lg C + \lg s_{r,2}^o \tag{2a}$$

where $p = 1 - k$.

C. Reliability of Results of Analyses of the Main Groups of Substances

1. Characterization of the Problem

The study of the values of intralaboratory and interlaboratory errors and their ratios on the basis of the generalization of sufficiently massive data began apparently in the late 1940s and early 1950s. The degree of reliability actually assured in 1965 to 1970 for the results of analysis of several groups of industrial raw and manufactured materials has been examined[2] and the conclusions of experts are given and the numerical data have been summarized. These conclusions, as well as the comparison of parameters characterizing the actually assured accuracy with the requisite and standardized accuracy (see Section I.D.), have confirmed that in many cases the former is sufficient, this leading to undesirable technical and economic consequences.

Has the situation improved since then? The answer cannot be unambiguous. Finally, we have to consider the presence of two parallel processes: one — improvement of methods and instrumentation, development, and expanding employment of means for checking the accuracy of analytical results, (especially RMs) as well as the statistical control of the quality of analyses, certification of methods, and accreditation of laboratories; the other process — the increasing complication of the composition of the traditionally analyzed substances (for example, steels) and the emergence of new objects of analysis: complex alloys based on nonferrous metals which previously had not been used for alloying; materials employed in modern electronics; new types of mineral raw materials and organic products, substances to be controlled with the aim of protecting the environment; and many others. Additionally, an answer is required not of a general type, but specifically for each group of substances.

Substances, the reliability of analysis of which should be evaluated primarily, should include the most important materials which have a widespread application, as well as substances analyzed for environment protection and health care purposes.

Regarding the methods of analysis, we have to consider the tendency to replace classical methods with physicochemical and physical ones, to automate analytical monitoring using such methods and new instrumentation. Traditional methods should be studied also; they will continue to be employed as a means for the determination of compositon. Many of them are used in the calibration of complex analytical set-ups as well as for the determination of the composition of RMs. Finally, in order to evaluate the advantage of automatic monitoring we have to know the initial level of certainty.

Regarding the conclusions which can be drawn on the results of estimation, they should be based not only on the opinions of specialists and individual cases, but also on quantitative characteristics, the values of which have been determined by summarizing sufficiently massive data. Unfortunately, as has been noted (see Section II.B.1), such data are not plentiful and they are not so informative as may first appear. Despite this, conclusions, which can give some inklings, seem to be useful.

Summarization of data has been made.[2,7] A review is given below of the main results of these generalizations. Publications of recent years show that there are no grounds to alter the main conclusions.

2. *Ferrous Metals and Alloys*

It is expedient to begin the review with ferrous metals and their alloys since data on these are plentiful and it is possible to discuss the relevant regularities.

a. Industrial Field Analyses

As early as the 1950s it was noted that the actual values of errors, characterizing scattering of data in parallel determinations ("wet" methods) performed by one analyst, are, as a rule, less or equal to those corresponding to official norms.[62,70,72] This is easily explained: if similar data differ by more than tolerated by norms, they are suppressed and measures are taken to correct the situation. With this in view, the upper limits of such errors may be taken as equal to values calculated in accordance with norms for tolerable discrepancies, stipulated, for example, in standards for analytical methods. The relationship between these values and the content under determination in the case of ferrous metallurgy products (also nonferrous metals, alloys, and several groups of mineral raw materials) is presented by Shaevich.[2,12] The corresponding mean dependence is shown in Figure 1 (curve 1). The results of massive investigations[73] carried out in the middle 1970s confirm the following: in Figure 1, curve 2, plotted on the basis of data processed by Pliner et al.[73] practically coincides with curve 1.

The value $s_{r,1}$ varies within 0.6 to 1.8 for determinations of various elements in cast irons and steels (the higher values belong to elements which are determined with greater difficulty). The coefficient p in the case of the more simple determinations is close to 0.5. For more complex determinations it fluctuates within wider limits,[4] remaining on the average close to 0.5. In addition to curves 1 and 2, curves 3 and 4 are also shown in Figure 1. The difference between curves 1 and 2 and 3 and 4 may be explained by the insufficient representativeness of data or actually differing levels of accuracy ensured under various conditions.

Because of the wide use of emission spectrochemical analysis methods it is of interest to evaluate respective data. For methods featuring photographic detection of the spectrum the value of $s_{r,1}$ (pertaining to intralaboratory deviations) according to many investigations varies within 2 to 7%. The utilization of special techniques, highly stable spectrum excitation sources, and precision spectrum detection apparatus in conjunction with a thorough preparation of specimens makes it possible to reduce $s_{r,1}$, even when analyzing high contents down to 1% (Figure 1, curves 5 and 6). For methods with photoelectric detection, dependence

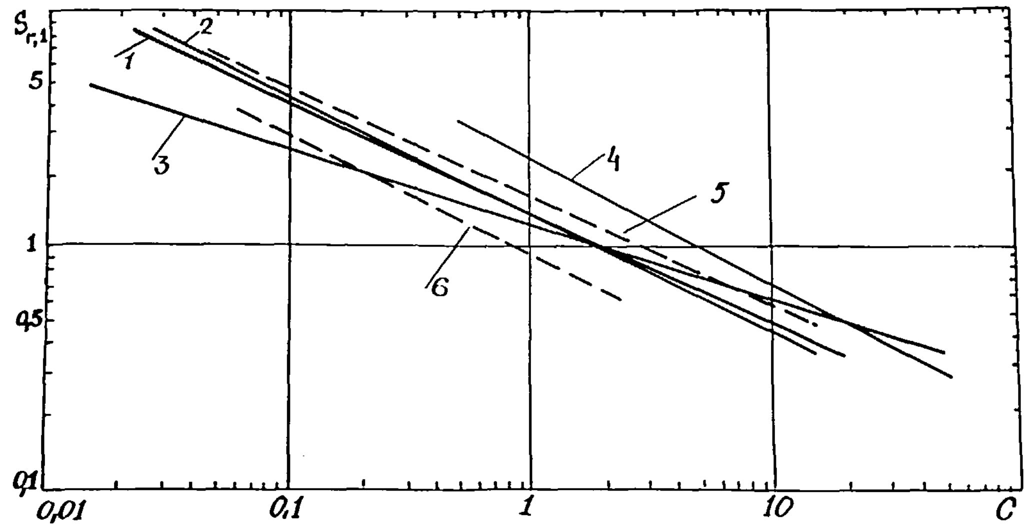

FIGURE 1. Relationship $s_{r,1}$ vs. C for field analyses of ferrous metals. (In this and following figures, please refer to the relevant part of the text for the meaning of numbers and sources of information).

5 is typical. The latter has been obtained by processing the data of 4300 comparisons of results of field analyses with those of chemical check tests. This dependence pertains to the analyses of carbon and low- and high-alloy stainless steels.[76] These data are apparently somewhat overrated since they include the errors of the results of check tests. Dependence 6 pertains to a later period (quantometric analysis of carbon steels).[77]

Regarding interlaboratory errors typical for industrial field analyses, there is very little published information on direct experiments. There are some generalized estimates for not only ferrous, but also nonferrous metals and alloys, as well as nonmetallic substances (ores, slags).[74] These data, concedes Püschel,[74] are not very representative. Besides, Püschel does not state whether these data pertain to field or precision determinations. Estimates are reported[7,78,79] which belong to a set containing about 700 mean results of interlaboratory experiments, (200 of which are listed in RM certificates) and about 1500 results, the processing data for which are set forth in ASTM standards E350-70 to E353-70. Approximately 90% of these results are typical of field analyses. Therefore, one may assume that they are sufficiently representative. The obtained estimates of parameters in equation 2a are as follows (content intervals and percent are given in brackets)

1. Gravimetric method (0.01 to 10) $s^0_{r,2} = 1.6$, $p = -0.37$
2. Titrimetric method (0.001 to 10) $s^0_{r,2} = 2.3$, $p = -0.20$
3. Photometric method (colorimetry and spectrophotometry) (0.001 to 10) $s^0_{r,2} = 1.8$, $p = -0.30$.

Mean values: $s^0_{r,2} = 1.9$, $p = -0.29$. The relationship between $s_{r,2}$ and C is presented in Figure 2 (dependence 1).

The generalized data given by Lewis[80] also refer to the analysis of both ferrous and nonferrous metals (with no subdivision). Each element was determined by approximately a dozen laboratories. Attention was given to differences between laboratories using standardized methods (atomic absorption analysis, photometry with and without preliminary separation). The results obtained for all the variants did not differ greatly (especially taking into account the confidence limits). The generalized results obtained by processing data[80] are shown in Figure 2 (dependence 2) by coordinates used here. It is interesting to note that

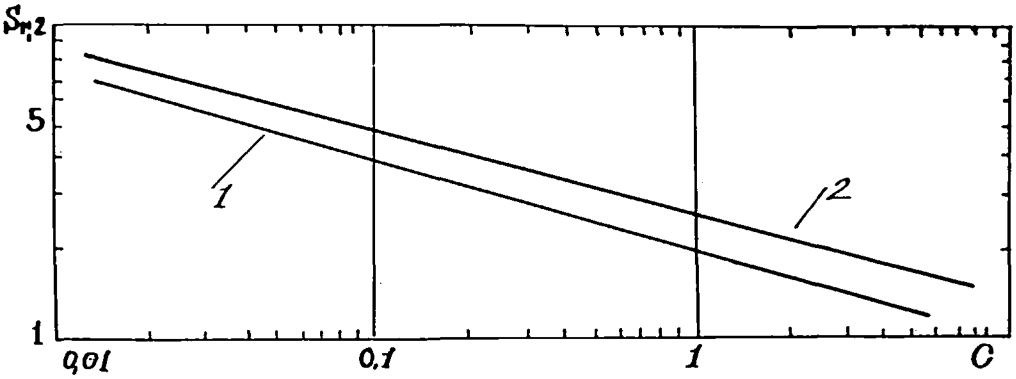

FIGURE 2. Relationship $s_{r,2}$ vs. C for field analyses of ferrous metals.

estimates of the parameters of the constraint equations obtained independently in various countries (curves 1, 2) are close to one another.

The ratio of $s_{r,2}$ to $s_{r,1}$ is of interest. Here two sources of information are possible. First, we can select the more typical dependences for $s_{r,2}$ and $s_{r,1}$ and use them to calculate the ratio for the relevant content interval. Second, we can use data on this ratio given in various publications. In the latter case we can use in principle the less typical dependences also, since in spite of differences between $s_{r,2}$ or $s_{r,1}$ and typical ones, the effect of these differences to a certain extent is smoothed out through the use of the ratios of quantities. With estimations made according to the first method, the dependence described by practically coinciding curves 1 and 2 (Figure 1) is typical for $s_{r,1}$ and curves 1, 2 (Figure 2) for $s_{r,2}$ when chemical methods are used. Taking this into consideration we can estimate the ratio $s_{r,2}$ to $s_{r,1}$ for contents in the vicinity of 0.01% = 0.5; for contents of 0.1% = 1.0; for contents of 1% = 1.5; and for contents of 10% = ~2.5.

b. Precision Analyses

Valuable information can be obtained through the processing of representative data from determinations carried out in the course of the development of RMs. The average values of the entire set (about ten) of elements for $s_{r,1}$ was 1.6% in 1954 (Shaevich[62]), 0.9% in 1972 (Dousier et al.[78]) and 0.9% in 1976 (Pliner et al.[81]) A similar processing of data contained in the same papers yielded the following values for $s^{o}_{r,2}$: 1.7% (1954), 1.4% (1972), and 1.1% (1976). We can assume, therefore, that in the course of the last two or three decades intralaboratory errors of analysis of ferrous metals and their alloys have been reduced almost twofold, while interlaboratory ones have been reduced one and a half times.

Finally, another group of important generalized estimates can be obtained by comparing selected typical values of $s^{o}_{r,2}$ and $s^{o}_{r,1}$, which are characteristic of industrial field and precision analyses. This comparison shows the following. For industrial field analyses the ratio $s^{o}_{r,2}$ to $s^{o}_{r,1}$ is equal to about 1.4; for precision analysis $s^{o}_{r,2}$ to $s^{o}_{r,1}$ was equal to 1.0 (early 1950s), 2.0 (1972), and 1.0 (1976). The ratio of $s_{r,1}$ values for industrial field analyses to those for precision ones was 1.1 (1950s to 1960s), 0.5 (1972), and 0.7 (1976). Herewith, the value of $s^{o}_{r,1}$, calculated on the basis of tolerable discrepancies stipulated in standards for methods of anaylsis, remained stable and equal on the average to 1.4. The ratio of $s_{r,2}$ values for industrial field analyses to those for precision analyses was 1.3 (early 1950s and in 1972). According to the 1976 estimates it was 1.6. The reciprocals characterizing the safety margin of precision analyses are equal to 0.8, 0.8, and 0.6, respectively.

In conclusion we can note the following in regard to the analyses of ferrous metals and their alloys. The use of various methods (if they are well tried) and laboratories (which have

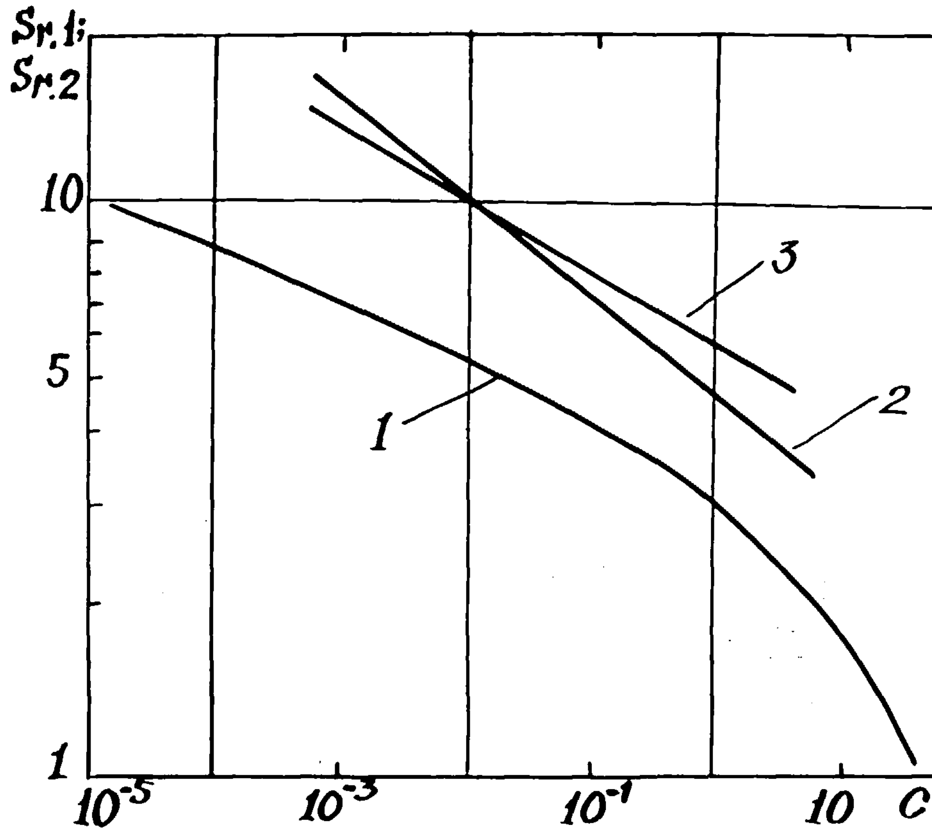

FIGURE 3. Relationships $s_{r,1}$ vs. C and $s_{r,2}$ vs. C for analyses of nonferrous metals and alloys.

sufficient experience in the utilization of these methods and the systematically employment of RMs) assures practically equal reliability (within the range of contents for which each of the methods is intended). The reliability of results of determinations of most elements are close to one another, although individual differences do exist. The ratio of interlaboratory to intralaboratory errors is apparently minimal in comparison with similar data for other objects.

The method of analysis of the situation considered above may find use in similar investigations of other groups of substances.

3. *Nonferrous Metals and Alloys*

For estimating the upper level of intralaboratory errors we can make use, as in the case of ferrous metals and their alloys, of generalized data on the tolerable discrepancies stipulated in a number of national standards (Figure 3, curve 1 characterizing mean values).[2,12]

Regarding interlaboratory discrepancies, reports were published in 1973 on data results[8,9] (about 300 mean results), as well as of more than 1000 mean results of the certification of RMs and more than 600 mean results presented in ASTM standards E34-68, E39-71, E120-69, E354-70, E355-70, and in the French standard NF 10-003. Thus, these summarized data characterized a certain level, intermediate between those which pertain to industrial field and precision analyses. The estimates of the equation parameters are as follows (range of contents and percent is indicated in brackets): $s^{o}_{r,2} = 5.5, p = -0.13$ for the gravimetric method (0.01 to 60); $s^{o}_{r,2} = 4.1, p = -0.22$ for the titrimetric method (0.001 to 60); $s^{o}_{r,2} = 4.8, p = -0.18$ for the photometric method (0.001 to 40); $s^{o}_{r,2} = 4.8, p = -0.08$ for the emission spectrochemical method (0.00005 to 1); $s^0_{r,2} = 5.9$ $p = -0.11$ for the atomic absorption method (0.00005 to 1). The mean values are $s^0_{r,2} = 5.0$, $p = -0.16$. For the narrower content ranges, namely within 0.001 to 5% (photometric method), 0.001 to 0.1% (emission spectrochemical), and 0.00001 to 0.1% (atomic absorption method), the values of $s^0_{r,2}$ diminish somewhat: 3.5, 4.7, and 4.8%, respectively.[79] The generalized dependence corrected for this circumstance is presented in Figure 3 (curve 2). The mean value of $s^0_{r,2}$ is 4.5%.

In 1976 data were published[80] characterizing the actually assured accuracy of analyses with the use of atomic absoprtion spectrophotometry and standardized photometric methods (with or without preliminary chemical separation). Unfortunately, as has been mentioned, analytical data for ferrous and nonferrous metals and their alloys have not been separated. The average values, describing the interlaboratory differences are presented in Figure 3 (curve 3). Although data[78-80] pertain to substantially differing sets, the positions of curves characterizing the relationship between $s_{r,2}$ and C are close to one another. It is important to note that not only the values of $s_{r,2}$ are close to one another, but so too are those of p.

4. *Mineral Raw Materials and Substances of Equivalent Complexity*

This group includes mineral raw materials and substances of equivalent analytical complexity such as rocks, concentrates, slags, refractories, and cements.

Summarized data were published[7,78] characterizing the results of analyses of mineral raw materials made in different laboratories. Use was made of papers published in the 1960s as well as other data,[83-86] including ASTM standard E278-67 and the results of certification of RMs (in all about 39,000 results). Most of these results can be classified as precision analyses. The estimates of the Equation 2a parameter are as follows (the range of contents and percent are indicated in brackets): $s^0_{r,2} = 4.0$, $p = -0.20$ for the gravimetric method (0.01 to 80); $s^0_{r,2} = 4.3$, $p = -0.22$ for the titrimetric method (0.001 to 60); $s^0_{r,23} = 8.3$, $p = -0.14$ for the photometric method (0.0001 to 20); $s^0_{r,2} = 10.5$, $p = -0.15$ for the optical emission spectrochemical method (0.0001 to 20); $s^0_{r,2} = 9.1$, $p = -0.06$ for the atomic absorption method (0.0001 to 20); and $s^0_{r,2} = 7.8$, $p = -0.10$ for the activation method (0.00001 to 4). The dependence averaged over all the methods is shown in Figure 4 (curve 1). For data pertaining to the precision analysis of ferrous metal ores, refractories and slags (issue of RMs),[4] the average dependence is shown in Figure 4 (curve 2). For data on the analysis of ores and rocks refer to Lontzikh and Berkovitz[87] and Falkova et al.[88]

5. *Chemical Products*

The monitoring of the purity of chemical products is affected by the determination of content of impurities of the main substance. A typical case of determination of impurities is the analysis of special-purity nitric acid by the emission spectrochemical and flame photometry methods.[89] It has been discovered that in various laboratories the same specimens in the content range of 10^{-7} to 10^{-3}% exhibit variations in analysis results most often of 150 to 50%, respectively. The ratio $s_{r,2}$ to $s_{r,1}$ is about 6.

A thorough investigation[90] has been made of the sampling and analysis of fertilizers. This paper, although published many years ago, can be recommended for its plan of a methodically correct and complete experiment. The results presented give an objective picture with such details as the consequences of sampling by various persons or the difference in the results of analysis of a sample in a given laboratory at different times. It is shown that the greatest scatter is observed for results obtained in different laboratories. The next in significance is the difference in results obtained in a laboratory in various periods (at a week's interval), then comes the difference in results obtained in a laboratory in the course of a day. Similar conclusions, drawn on the results of analyses of superphosphate are made by Malishkov et al.[91]

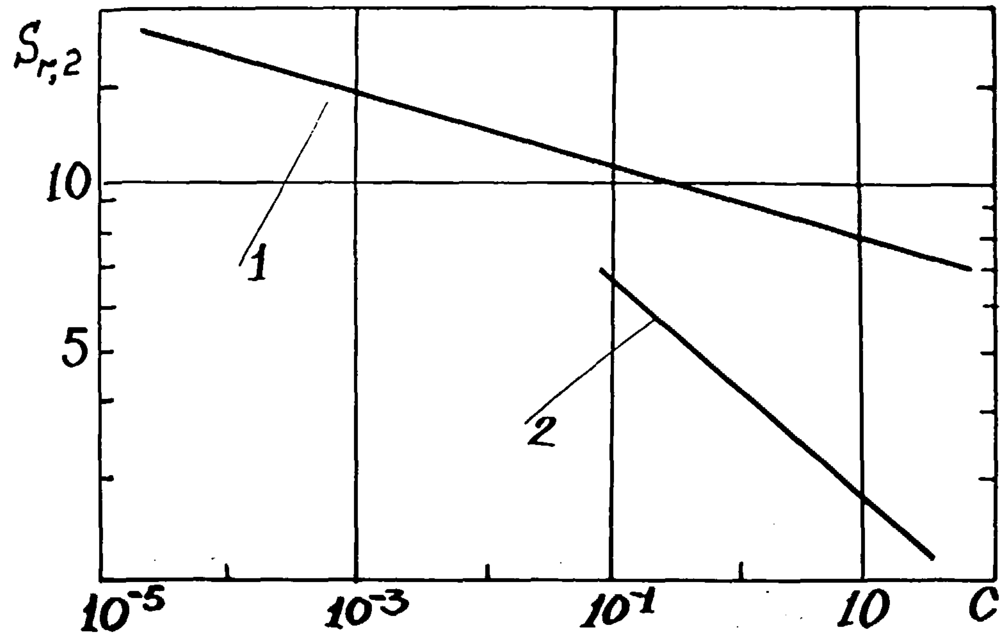

FIGURE 4. Relationship $s_{r,2}$ vs. C for analyses of mineral raw materials and substances of similar complexity.

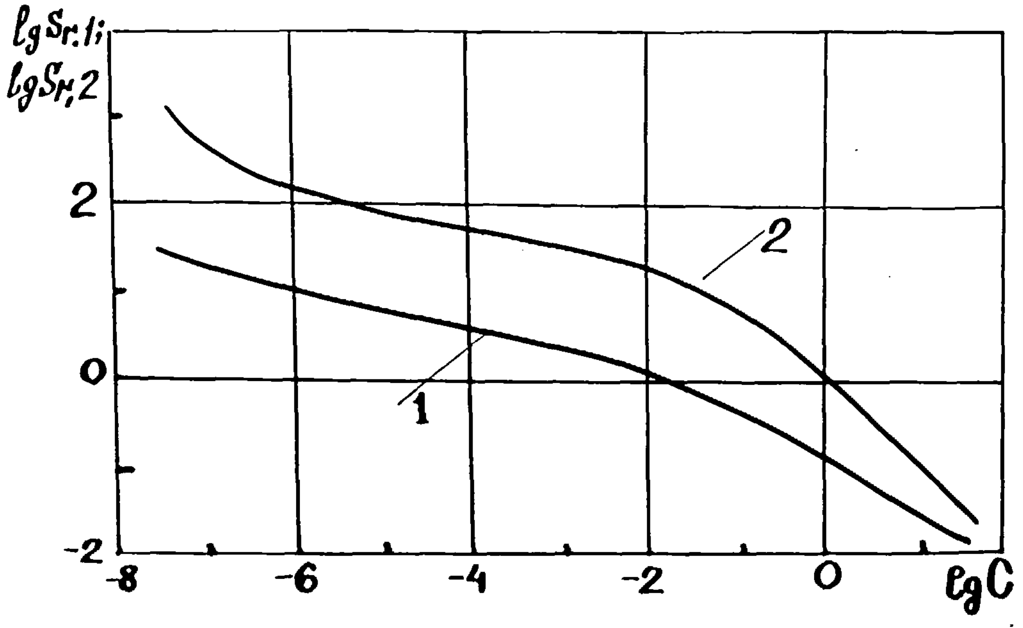

FIGURE 5. Generalized estimate of relationships $s_{r,1}$ vs. C and $s_{r,2}$ vs. C for analyses of chemical engineering products.

A generalized estimate of values $s_{r,1}$ and $s_{r,2}$ in a wide range of contents for the analyses of inorganic chemical products is presented in Figure 5.

6. Pollution of the Environment

The reliability of data pertaining to the state of the environment must be ensured in two general cases: when the initial state of the environment or of the region (e.g., level of background concentrations) is being established; and when the current state is being compared with the initial state. In the first case the reliability of the value of $\overline{C}_0$ is important ($\overline{C}_0$ is the quantitative characteristic of the initial state). In the second case the difference $\overline{C} - \overline{C}_0$ is of interest ($\overline{C}$ is the quantitative charcteristic of the state being compared with the initial one). If the difference between a certain state and $\overline{C}_0$ in regard to its consequence is considered to be permissible, then we can characterize this state by a certain norm $\overline{C}_{0,lim}$ (e.g., the maximum allowable concentration MAC). In such a situation it is required to assure the reliability of $\overline{C} - \overline{C}_{0,lim}$. The metrological aspects of these problems directly connected with analytical ones are considered elsewhere.[7,92,93]

When estimating the values of $\overline{C}_0$ and $\overline{C}$ for the environment as a whole or its regions it is necessary to assure the reduction of those parts of the errors in the final result which are due to the incomplete correspondence of sampling (specimens) to the parameters of the general set. In particular cases, for example, in monitoring sewage after purification, this component of the overall error may be substantial. Below we consider that part of the overall error which pertains to the analytical results.

The allowable levels of pollution are usually not high. Under these conditions the relative error of the analytical results increases as compared to "usual" determinations. Moreover, the experience of the metrological services in this field is comparatively meager, while the complexity of substances under analysis is considerable and there is still no effective system of monitoring the accuracy of the results. All of this makes the problem in this field very significant.

It has been proposed to divide analytical methods used in monitoring the pollution of water into three classes depending on the value of the overall error:[94,95] if this value is less than 25%, the method is excellent, if it is not >50%, the method is acceptable, and if the value is >50%, the method is unacceptable. With the purpose of assessing the quality of various methods in accordance with these criteria, an analysis was made of water samples with known (specially introduced) contents of impurities. Of the 27 mean results of the determinations of 9 metallic elements, 23 were found to be too high; of 15 mean results of the determinations of 15 pesticides, 14 were found to be too low.[94] It was demonstrated that the determination of pesticides is characterized by an overall error 2 to 3 times as great as that obtained in the analysis for metals. The results[94] pertain to model solutions. In practice, much more complex compositions are encountered with consequent increase in analytical errors. A typical example is provided by[96] determination of components in samples of water containing known (specially introduced) mass concentrations (mg/ℓ) of nitrate nitrogen, soluble reactable phosphorus, and soluble general phosphorus. Twenty-three laboratories took part in the experiment using generally accepted analytical methods. The investigated set consisted of the mean results of several parallel determinations carried out in each laboratory. The data processing results are presented in Figure 6.[7,92] They serve to illustrate important features. As in many other cases the errors are substantially higher than usually expected. Their distribution is asymmetrical; they are best described not by a normal, but by a logarithmic-normal law. Hence, confidence limits for the analytical results are likewise asymmetrical; they are for a confidence probability of 0.95 equal to 30 to 50% in the negative range and 200 to 400% (and more) in the positive. The above results agree with those[97] pertaining to the determination of petroleum and oils in water. For the gravimetric method and the same confidence probability the errors are 37, 70, and 97% in the negative range and 58, 300, and 3700% in the positive; in the case of infrared spectroscopy the errors are 23, 33, and 44% in the negative range and 23, 40, and 80% in the positive. These data relate to concentrations of 100, 15, and 1 mg/ℓ, respectively, in artificial samples.

The insufficient level of the reliability of results of analysis of polluted water, especially in the region of relatively low contents, has also been noted by many researchers[98-106] This

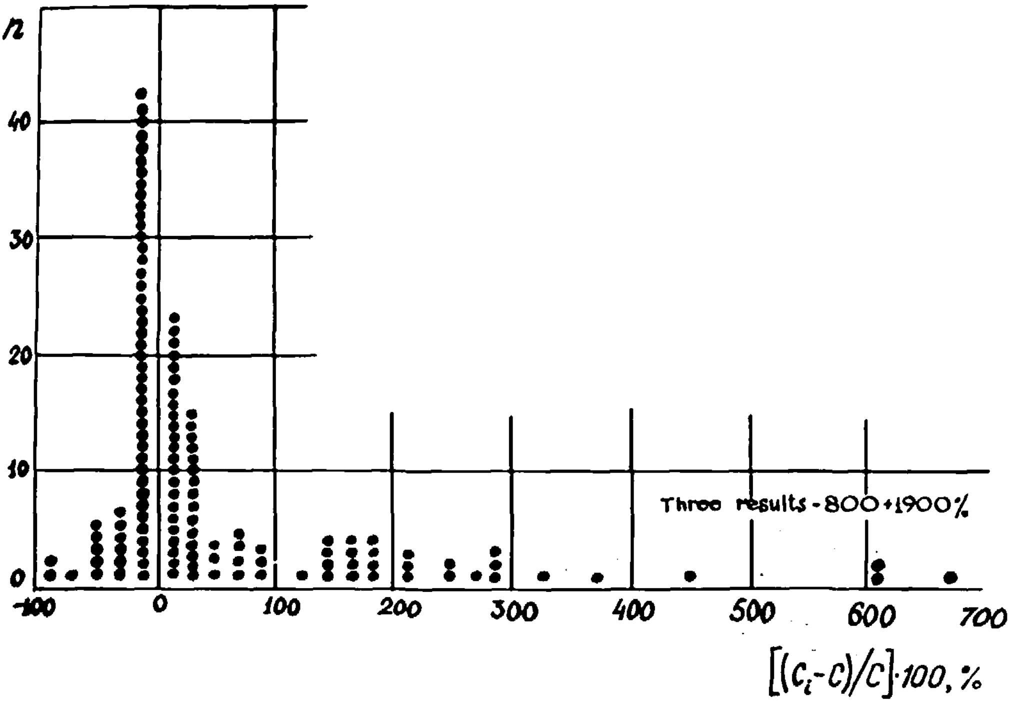

FIGURE 6. Summary diagram of distributions of the values of $[(C_i - C)/C]$. 100% obtained in an interlaboratory experiment (analysis of water for content of nitrate nitrogen, of reaction-capable and soluble general phosphorus: C_i is the mean analytical result of i-th laboratory, C is the actual content: n is the number of mean results).

circumstance, in conjunction with the necessity of establishing a system of sampling, and in certain cases new analytical methods, has been the cause of initiating programs for the purpose of obtaining realistic estimates and improving the situation.[107,108] A similar situation is characteristic of monitoring air pollution.[109,110]

Available data confirm the fact that the determination of low concentrations is more reliable by means of physical and physicochemical analytical methods than with classical ones. However, it should be borne in mind that considerable errors remain in the latter case too, that is, we are not freed from troubles responsible for systematic errors, especially with mass monitoring. Consequently, data on the high accuracy of results obtained through the use of physical methods, for example, X-ray spectral fluorescent analysis of objects monitored for the sake of safeguarding the environment,[111] should be regarded with some doubt.

Regarding the reliability of the difference $\bar{C} - \bar{C}_0$ (see the beginning of this section) with no systematic discrepancies in the determination of $\bar{C}$ and $\bar{C}_0$, the random error of the difference grows, as is known, $\sqrt{2}$ times, if the determinations of $\bar{C}$ and $\bar{C}_0$ are of equal accuracy. But analyses for the evaluation of $\bar{C}$ and $\bar{C}_0$ are performed at different times and, often enough, by various methods (e.g., determination of trace elements in aquatic media both prior to and following intensive pollution). In such cases the possibility of systematic errors must be examined with special attention.

7. *Some General Regularities*

Attempts made to establish general regularities relating to actual values of errors in the results of analyses are complicated not only by the multiplicity of the problem, but in many cases by the lack of initial data. Such an attempt may, however, yield some useful information. When reviewing summarized data it should be borne in mind that they characterize

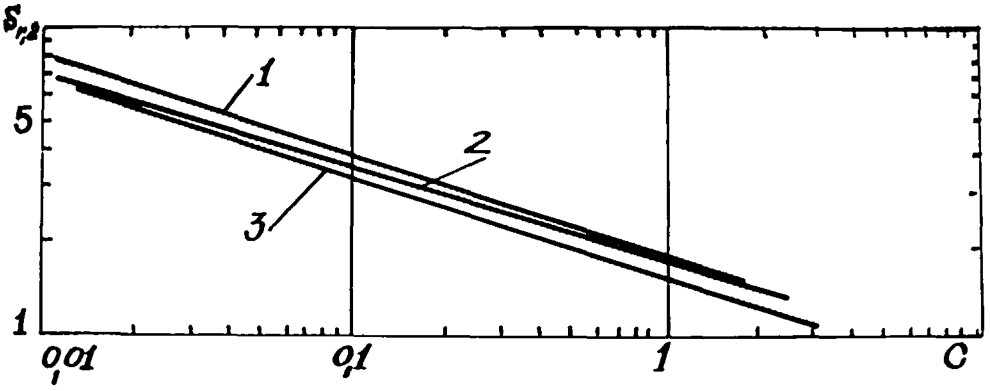

FIGURE 7. Relationship $s_{r,2}$ vs. C for analyses of ferrous metals by various methods: (1) gravimetric; (2) photometric; (3) titrimetric.

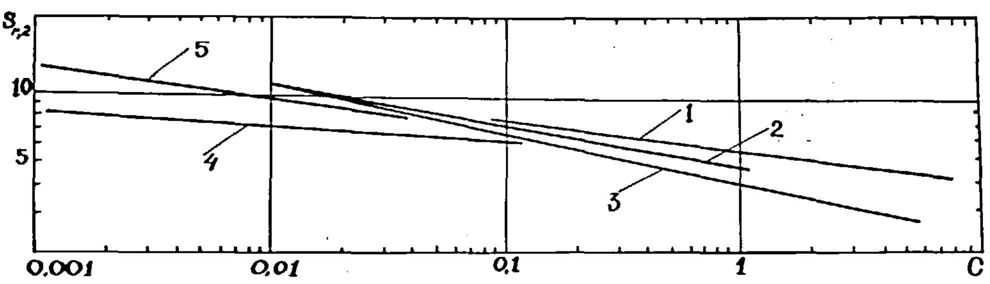

FIGURE 8. Relationship $s_{r,2}$ vs. C for analyses of nonferrous metals and alloys by various methods: (1) gravimetric; (2) photometric; (3) titrimetric; (4) emission spectrography; and (5) atom-absorption spectrochemical.

only a certain mean level pertaining to some or other condition. They should not be given significance more than that usually given to average values.

First, it is appropriate to examine whether differences exist in errors of the determination of various elements by one and the same method in one and the same group of substances of similar analytical complexity. The generalization of data pertaining to inorganic substances suggests that such discrepancies in most cases are small; the estimates of relevant parameters differ by not more than 1.5 times. With this in view, it is hardly possible to assume that substantially differing allowable discrepancies, set forth in instructions of various origins for the determination of different elements in the same content range by one and the same method in substances of similar complexity, are justified.

Second, we must discuss whether it is possible to assert that the use of various methods in the analysis of one and the same substance leads to results differing with regard to precision or accuracy.

Data presented in this section show that the answer cannot be unambiguous. Thus, the examination of three analytical methods of inorganic substances, i.e., gravimetric, titrimetric, and photometric methods, (photocolorimetry and spectrophotometry) leads to the following conclusions. In the analysis of ferrous metals and alloys the discrepancies are practically insignificant (Figure 7). The discrepancies in the analysis of nonferrous metals and alloys, although they are somewhat higher, are not very large (Figure 8). In the analysis of mineral raw materials and analytically similar substances, substantially lower interlaboratory discrepancies are observed if gravimetric and titrimetric methods are used (Figure 9).

We should not forget that every analytical method should be used in its optimum range

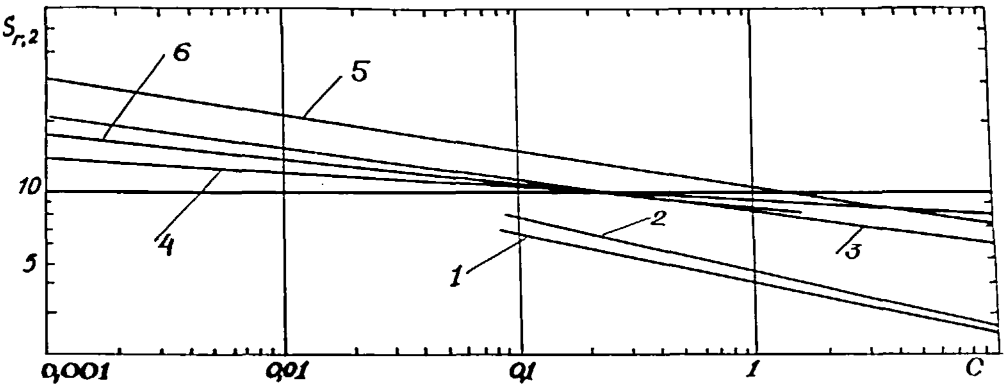

FIGURE 9. Relationship $s_{r,2}$ vs. C for analyses of mineral raw materials and similar substances by various methods: (1) gravimetric; (2) titrimetric; (3) photometric; (4) atom-absorption spectrochemical; (5) emission spectrography; (6) activation.

of contents. Thus, gravimetric methods are less suitable for the determination of low contents. Hence, it is always important to indicate not only the method, but also the range of contents when we are speaking of errors. The use of the concepts "mean method", "mean element", and "mean material", suggested as generalized characteristics,[72] may lead to false conclusions if these notions are not employed in a precisely defined context. Indication shall be given as to what methods are included in the considered group, whether each of these methods is used in its optimum range of contents, what groups of substances are being analyzed, etc.

There is insufficient initial information for drawing conclusions on the analytical methods of organic objects, including those of a biological nature. It is known, however, that sometimes the employment of various methods gives results differing several-fold, as in the case of clinical-chemical analyses.

Despite the fact that certain regularities can be traced in the values of quantities characterizing precision and accuracy attained with various methods, we should be careful in the interpretation of such a statement as "this method is more reliable than that". The quality of results depends, as experienced analysts know, not only on the potential possibilities of a method, but also on the actual working conditions in each laboratory.

When examining the errors of analytical methods one should note any distributions which differ considerably from the normal (Gaussian) distribution. Attention was drawn to this long ago.[63] Such distributions occur often enough especially in the analysis of small contents and in the determination of analytically complex objects.[2,7,65,92,98,112] The occurrence of asymmetrical distributions testifies to a real danger of the appearance of errors, the values of which greatly exceed the "usual" ones. The general causes of asymmetrical distributions, not only in the range of low content values, but also in the vicinity of 100% content, are discussed elsewhere.[7] It is shown that it is not only the smallness of content that is important, but also the ratio of error to content. For example, if the gravimetric method for the determination of not very low contents were to be used, (about hundredths of a percent), there would also be an asymmetrical distribution of errors. (The relative error in such a situation would be 30 to 50%.) With contents close to 100%[7] it is not only the content value that is important, but the ratio of error to the value 100%—C (where C is the content percent).

The thesis has been expounded that the metrological characteristics of methods based on calibration cannot be better than those which characterize the classical analytical methods, since the calibration means (RMs, for example) are certified in the end by classical methods.[10]

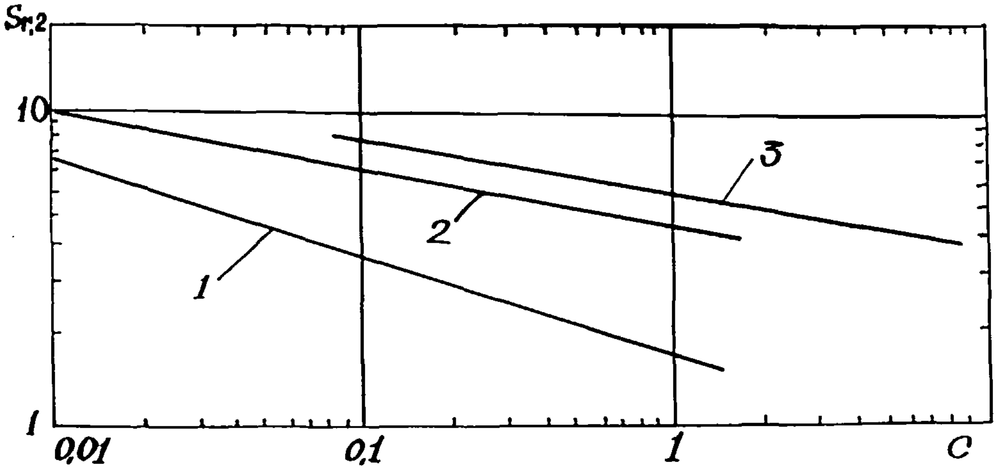

FIGURE 10. Generalized estimate of relationship $s_{r,2}$ vs. C for analyses of: (1) ferrous metals; (2) nonferrous metals and alloys; (3) mineral raw materials and similar substances.

The data presented above do not confirm this point of view: in certain content intervals physicochemical and physical methods have advantages. This can be explained by two causes:[11] (1) it is possible in a number of cases to establish the content of RMs and similar means not by analysis, but by calculation (in accordance with the preparation procedure) and (2) since for calibration several RMs (or similar means) are used, the certification errors for each of them may be averaged (compensated for).

If we were to compare the analytical errors of various large groups of substances, a distinct tendency would be observed in the case of inorganic substances; the least interlaboratory errors are characteristic of the analysis of ferrous metals and alloys, the greatest errors are characteristic of nonmetallic substances such as mineral raw materials and similar objects. Nonferrous metals and alloys occupy an intermediate position (Figure 10). This can be explained by the different levels of complexity of each of these groups of substances, considered as objects of analysis (in the case of nonmetallic systems there can also be the difficulty of producing homogeneous samples), as well as by the different stocks of RMs (means of controlling the accuracy of results) available. Analytical systems insufficiently ordered from the metrological point of view exhibit a poorer accuracy: the ratio $s_{r,2}:s_{r,l} \geqslant 3$.

Examining the variation of errors vs. content, it is important to take into account not only the free term in Equations 2 and 2a, but also the slope p, since the latter determines the rate of growth of errors as the analysis involves lower and lower contents. According to Pliner et al.[81] the value $p = -0.5$ is typical for metrologically ordered analytical systems (good methods, availability of RMs and their effective use). At the same time, values of p of approximately -0.2 and -0.3 (considerably differing from 0.5) have been noted for the same systems. In order to ascertain whether such differences have anything to do with the processing of results, one and the same set of data was processed by four methods.[76] The most exact is the method which takes into account that estimates of values of not only s_r, but also of C, are established with a certain error. Hence, it is best to calculate the estimates of values of parameters k and s_r^0 in Equation 1 as recommended by Robinson and Lott.[113] However, the use of these or other data processing methods does not lead to such great differences in parameter p, which could explain the discrepancy. This matter still has to be cleared up.

As to the variation of analytical errors with time, there is a tendency for their diminution in the case of inorganic analysis. The chief cause of this is the widespread use of physicochemical and physical methods and their further development (for contents of several percent and lower). When a method has no strong competitor (e.g., the gravimetric method at the content level of several tens of percent) the tendencies to improve are slight in the case of precision analyses, while in the area of industrial field analyses there is some correlation with the stock of RMs available in the laboratory.

8. *The Consequences of Insufficient Reliability*

The comparison of data characterizing the actual errors in analytical results with tolerable values (calculated in accordance with the norms of contents in standards for materials) shows that the former, according to conservative estimates, are 2 to 3 times greater than the latter. The concrete technical, economical, or other (ecological, health) consequences of this fact are difficult to express quantitatively. At the same time generally unfavorable consequences have been observed.[2,3] Thus, in order to compensate for the errors of analysis of technologically important materials, the suppliers and consumers are forced to increase the number of tests of their properties, (namely mechanical, physicochemical, and other properties) as well as tests for the reliability of products manufactured from these materials. Manufacturers have to introduce systems of "internal" tolerances of their own for composition, more stringent than the official ("external" ones, for example are those stipulated in standards on materials). The higher the analytical errors the narrower the tolerances for composition must be, as compared to the "external" values. This leads to additional expenses, for it is necessary to ensure better quality raw materials at the input of the technological process or provide for their purification in the course of processing. If the feasibility of maintaining narrower tolerances for composition is limited because of analytical errors, the batches of manufactured materials are often characterized by higher discrepancies in composition, hence, in properties with the ensuing consequences. The latter may lead to the increase of safety margins of constructional materials or may be hidden from view for a time, but producing an adverse effect in the course of service of the product. Similar conclusions can be made concerning the estimation of mineral deposits, ecological, and health problems.

Quantitative models and methods useful in the calculation of technological and/or economic consequences of that or other levels of reliability of analytical results are described by various authors.[2,7,16,114-121]

III. DEMONSTRATION OF THE ACCURACY OF THE RESULTS OF FIELD ANALYSES

Although this section is devoted to field analyses, some of the inferences can be implemented in higher-level analyses. I shall also discuss methods, but in practice everything said can be applied to analytical instrumentation systems since underlying the functional scheme of each analytical instrument (even one operating without a human operator, e.g., gas analyzer, automatic titrator, etc.) is a certain methodical principle.

The topics discussed in this section are closely related to certain problems examined by various authors,[3,6,7,22] however statistical control of the quality of analyses and corresponding calculation methods are not discussed here.

A. The Main Sources of Errors

The general classification of errors (random, systematic, gross) has been expounded and discussed in numerous textbooks on metrology. Lately in such publications it has been more and more emphasized that errors can pass from one class to another depending on the circumstances, and that often, in order to estimate noneliminated systematic errors, as well as the overall error of the measurement result, the probabilistic approach has to be made. The specific features of quantitative chemical analysis have led many authors to the same conclusions.

In this section we shall not examine the sources of error which are peculiar to certain specific methods.[1] We shall, however, review their most common sources. This is of interest by itself, in addition to being necessary for the elucidation of the possibilities and limitations of various techniques of proving the accuracy of analytical results.

Methods which are considered sound are usually those implemented in the laboratory. Already at this stage at least three types of errors according to sources may show up and remain in subsequent field analyses. The first type includes errors which are inherent in the method itself. They are usually due to insufficient awareness or incomplete consideration during the development of the method of all the circumstances which may distort the results of analyses carried out by this method. Another type of error is the nonconforming use of a method, that is, employment of the method for the analysis of substances which are not sufficiently similar from the analytical point of view to those for which the given analytical method has been primarily intended. The following quotation[9] is illustrative: "written specifications of methods of measurement often contain absolutely precise instructions which, however, cannot be carried out repeatedly with complete exactitude in practice...". In quantitative analysis examples of such instructions are "heat until sulfuric acid vapors are in evidence", or "heat slowly", etc. The third type of error is the one occurring at the "input" (a suitable and well described method having been selected). This error is due to the inhomogeneity of the analyzed samples (in regard to composition, sometimes physical properties, and structure) or their contamination with impurities.

At subsequent stages of analyses it has been proposed to distinguish errors of measurement and errors of procedure.[1] The first stage includes errors associated with measurements themselves (weighing, measuring volume, measuring radiation intensity, etc.). The second stage includes those that occur for purely analytical reasons (e.g., incomplete reaction). Such a classification should be viewed with some caution. Each analysis, with regard to its general aim is, on the whole, a measurement procedure (see above) and metrologists consider such procedure as consisting not only of individual measurements, but also of preliminary and intermediate operations required for their implementation.

Taking the above into account, it seems better to speak of operations and errors associated with apparatus (balances, burettes, etc.) and of those associated with the analytical procedures themselves (separation, concentration of components, their mutual effect, etc.). Among the sources of errors of the first type are nonideal quality of apparatus and nonideal performance of operating personnel (errors of adjustment, weighing, measurement of volume, radiation, and other parameters). Errors of the second type are more diverse and, as a rule, more important. Among these are (1) loss of analyzed and bothering components in the course of the analysis because of the incomplete character of chemical reactions and physical processes, dependence of such reactions and processes on circumstances that are not always easily controlled; (2) contamination of impurities from reagents and water of insufficiently high quality from the atmosphere of the laboratory; (3) individual qualities of the analyst (e.g., the ability to detect the end of evaporation, titration); and (4) insufficiently objective establishment of calibration characteristics (resulting from incomplete correlation between substances used for calibration and samples, also from faults of calibration means and procedures) and time drift of such characteristics including rounding off of numerical values.

Regarding checking errors (connected with control of accuracy), it is natural to expect[4] that checks (including self-checks) be objective. Insufficient high-quality checks are harmful in that they direct the work of maintaining the accuracy of field analyses along a false course or force one along the hard road of accuracy demonstrations. One of the sources of bias in checks may be that the quality of such means as RMs and substances of a similar purpose is not high enough. Errors impairing the qualities of such substances should be distinguished from those (usually more important ones) that are due to the poor correspondence between characteristics of these substances and analyzed samples. Finally, such a source of uncertainty is used for random inspection of accuracy. It is possible that errors may be due to the transfer of sampling estimates on the entire set to be controlled, if fully adequate sampling control plans are not used.

The detection of errors in a number of cases is affected by a critical review of the content of a method and conditions of its implementation. Following this, measures are taken to eliminate the errors. However, such a technique, although necessary by itself, does not always give confidence that the sources of all substantial errors have been detected and eliminated. A necessity arises to confirm the accuracy of obtained results after successive improvements are introduced. Thus, the proof of the accuracy of a method is an important problem at the stages of development, approbation, implementation, and the use of methods (instruments). Naturally, the approaches to the solution of this problem have a lot in common at all these stages, but there are also differences due to the diverse purpose of these stages such as different amounts of time and resources provided for obtaining specific results.

B. Summary of Techniques Used for Demonstration of Accuracy — Their Possibilities and Limitations

1. Repetition of Analyses

One of the recommendations given in a doubtful case is to "repeat the determination or series of determinations". In standards and instructions on analytical methods this recommendation is quite common and is often the only one. Its widespread use evidently reflects the point of view that analysis is an insufficiently stable process. This point of view has been formed in the course of long experience. It is based on the assumption that doubtful results (e.g., those differing considerably from one another) are the consequence of a relatively large statistical fluctuation, the probability of repetition of which is small. With regard to more considerable errors, (e.g., those inherent in the whole series of determinations carried out by an analyst practically simultaneously), there arises the problem of using more effective means. We can name a number of such techniques which have found more or less widespread application. A review is given below of their essence, possibilities, and limitations.

2. Use of Different Methods of Analysis

This technique is based on the assumption that there is a relatively low probability of equal (in sign and magnitude) errors if different analytical methods are used. Such an assumption is valid in principle and is usually justified. However, we have to consider two circumstances in this connection. First, the degree of the independence of results obtained under such conditions must be considered individually. Thus, nominally different analytical methods can have a stage that is common to all of them. In such cases methods cannot always be termed as different in the sense that there is a low probability of common errors. For example, the titrimetric and spectrophotometric methods may include a stage of decom position of the sample, proceeding alike, i.e., methods, although called differently, may differ only with regard to the end of the analytical process. Second, when we have differing results it is difficult to ascertain which of them is nearer to the true value.

3. Participation of Several Laboratories of the Same Level of Proficiency

The logical assumption of this technique, as that of the recommendation of repeating analysis carried out in one laboratory, is that there is a low probability of substantial errors equal in sign and close in magnitude if analyses are performed by one and the same method in different conditions (although this probability cannot always be disregarded). As has been noted already (Section II.B.1.) the following argument is methodically more correct: if the results of analyses carried out in various laboratories differ substantially, then a part of them or all of them are inaccurate; if such results are sufficiently close one to another, then this testifies to the fact that they are compatible, while the absence of error, common to all of them, must be proved.

4. Comparison with Data Obtained in a Highly Proficient Laboratory

The higher confidence placed in such data is based on the fact that in a high-proficiency laboratory the best methods are employed or more time is provided for analyses performed by ordinary methods and that the determination is executed by a more qualified staff who use reagents and apparatus of a better quality than in field laboratories. These assumptions are in each case justified to some degree, but this technique cannot be considered to be universal from the point of view of efficiency. In the light of data presented in Section II, including those characterizing interlaboratory errors when RMs are being issued (naturally, in this case the most trustworthy and approbated methods and the best analysts are employed), there are no grounds to think that the results obtained with even such methods are always as correct as necessary. Even if a "reliable" method has been monitored in its turn by means of RMs, for example, one should be very careful in using analytical data obtained with its help because of the possibility of accumulation of errors — a circumstance often overlooked.

When using reliable, trustworthy, and similarly described analytical methods, including standardized ones, one should bear in mind that they cannot be always be classified as reference ones (see Section III.B.5.). They are usually intended for obtaining more reliable results than could be obtained using ordinary analyses. However, an estimate is not always made of the actual level of accuracy. Assured by such methods, the optimum ratio between the errors of ordinary and check tests are not always discussed and maintained. Very often standardizing documents authenticating the allowable range in which a method may be used for monitoring the accuracy of results of field analyses of various substances are lacking.

5. Use of Reference Methods

From the metrological point of view, a reference measuring means is one intended for checking other measuring means and approved for this purpose. By analogy this definition may be applied to reference methods. Another less formal definition states that a reference method is one in which the accuracy has been checked and proved.[3,22,122] This definition seems to be too brief.

Accuracy can be checked and one can prove that it is characterized by a certain parameter, e.g., the value of noneliminated residual systematic errors. But the next step is no less important: to decide whether such an accuracy is acceptable or sufficient. Further, a reference method has to have not only a certain accuracy, but also precision (the latter is assured more easily). Finally, one has to be aware that the potential possibilities of a reference method, established in the laboratory responsible for the development of the method, and the actual realization of these possibilities in each of the laboratories using the said method are different things.

Taking the above into consideration it seems desirable to expand the definition[3,22,122] of a reference method as one which assures such measurement (analysis) results, the reliability of which has been checked, proved, and is found to be sufficient for a certain purpose; the quality of implementation of a reference method in specific conditions must be confirmed.

The idea of using such methods has been discussed often enough; it is advantageous to have methods, the utilization of which under approved conditions assures results which can serve as an official criterion of accuracy. The necessity for such methods has been actively propagated especially by metrologists who have gained experience in developing and applying them for purposes of physicochemical measurements, such forms as measurment of pH, moisture, gas analysis. However, such kinds of measurements of content are considerably less complex than the analyses of the majority of substances which are condensed systems (industrial solutions, mineral raw materials, most chemical engineering products, all metallurgy products, silicate materials, soils, etc.) requiring the "opening up" of the sample, separation, and concentration of many components and similar procedures. This complicates very much the development of reference methods.

The second aggravating circumstance is that the essence of the vast majority of analytical methods is such that they have to be differentiated very much depending on the composition of the analyzed substances. The great diversity of combinations of components forming the basis of various organic and inorganic substances and contained in the form of impurities, as well as the content ranges of these components force the analytical services to use thousands of modifications of ordinary methods. The number of reference methods and their modifications required for monitoring or similar purposes is also considerable.

Finally, we have to bear in mind that even having a sufficient number of methods and modifications, it is not a simple problem to provide conditions assuring the quality of reference methods in hundreds of laboratories engaged in the monitoring of ordinary analyses.

As a result, the analytical services use reference methods to a limited extent mainly for analyzing substances that are not very complex. All that has been said should not be regarded as an underestimate of the possibilities of reference methods in important fields or as a negation of the necessity of further development work.

6. *Use of Reference Instruments*

Reference analytical instruments have important fields of application, mainly for checking gas and liquid mixture analyzers. However, in these fields and in general their use is not free from limitations of technological or economical character. This is explained by a number of circumstances.

First of all, in the field of monitoring the accuracy of most types of industrial analyses, instruments alone are usually not enough for the checking. In the analyses of all solid substances and many liquid ones, one has to have RMs. In those fields where the use of reference instruments is possible their variety must be very great; practically for each type of field instrument, a reference instrument must be provided. This is difficult from the engineering point of view, as large capital investments and the employment of the best designers are required. Moreover, as it is often desirable to improve the metrological characteristics of field instruments, it is profitable to use each newly developed instrument intended for reference purposes as an improved field instrument — the problem remains again unsolved. Finally, for checking field instruments against reference ones it is usually necessary to dismount them from their operating site and transport them to the verification laboratory. This involves many inconveniences; one has to provide spare instruments to be used in place of those removed, facilities and personnel for handling and transportation, very often accuracy is lost on the return journey, etc.[123]

Because of all these difficulties, the stock of reference instruments remains limited, covering even in fields where their use is considered feasible in principle only 5 to 10% of the needs according to various estimates.

7. *Determination of the Sum of Contents*

This technique is based on the premise that if a complete analysis is made of a substance, the sum of the values of contents of all the components should be sufficiently close to 100%. The capabilities of this technique are limited. This is because a complete analysis is rarely carried out and also it is often difficult or impractical to monitor the contents of some components (for example, bound oxygen in minerals, ores, slags, and similar substances). From the metrological point of view this technique is not always effective, as a value close to 100% may result from the mutual compensation of errors in the summing up. In practice this technique may be of value in the converse variant; the derivation of a sum considerably less or more than 100% is an indication of inaccuracies in a part or in all the data. In the direct variant (derivation of a sum close to 100% as a test for accuracy) this technique is sufficiently effective in the analysis of relatively simple systems (for instance, two-component systems).

8. Use of the Material Balance of a Technological Process; Use of a Balance Sample

In the processing of raw materials in which C is the content of the monitored component, various products are produced and part of the component is lost together with the waste products. In this case the following equality shall hold

$$\sum_{i=1}^{n} a_i\hat{c}_i + \sum_{j=1}^{m} a_j\hat{c}_j = \hat{c} \tag{3}$$

where *n* and *m* are the number of products and wastes, respectively; $\hat{c}_i$ and $\hat{c}_j$ are estimates of contents (analytical results) of the i-th product and j-th waste, respectively; a_i and a_j are the so-called outputs of i-th product and j-th waste, respectively; $\hat{c}$ is the estimate of content C.

The nonfulfillment of this equality is an indication that it is necessary to check the accuracies of a part or of all the results. The closeness between the values of quantities in the left- and right-hand parts of this expression must not be interpreted, uncritically, as a proof of accuracy; a compensation of errors is possible in the determination of $\hat{c}_i$ and $\hat{c}_j$, as well as the existence of the overall error of values of $\hat{c}_i$, $\hat{c}_j$ and $\hat{c}$ (for instance, overrating of all the results). It should be remembered that coefficients a_i and a_j are experimentally determined quantities and their values also contain errors, very often considerable ones.

The so-called balance sample technique[124] resembles closely the previous one. In this case the analyzed sample is divided into several parts and each part is analyzed separately. The sum of the determined absolute values of the analyzed component must, to within a certain approximation, coincide with the quantity contained in an identical, but undivided sample. The subdivision of the sample must be carried out with sufficient precision, while the sample itself must be homogeneous enough. Remarks on the possibility of compensation of individual errors and the overall error made in connection with the technique of the material balance of a technological process hold true in this case, too.

9. Standard Additions Technique

To ensure the efficiency of this well known technique it is necessary to introduce additions at such a stage of the analysis that it is possible to check all the substantial errors (for example, those arising at the instant of opening up of the sample). Another, usually requisite, condition is the availability of the determined component in the addition in the same compound as in the sample being analyzed. The possibility of digression from these conditions must in every individual case be discussed.

The advantages and limitations of this technique are also discussed elsewhere.[125-129]

10. Variation of Sample Weighed Quantities

This technique is based on the analysis of different weighed quantities of the same sample. Let M_1, M_2,... M_i,... M_n be a series of increasing weighed quantities, where M_i is the mass of the i-th quantity. Let the amount of the component being determined in each of them (in grams, for example) according to the analysis results be: m_1, m_2,... m_i... m_n. In the absence of error proportional to the quantity of component being determined we have: $m_1/M_1 = m_2/M_2 = \ldots = m_i/M_i = \ldots m_n/M_n$. In the presence of a proportional error $m_1/M_2 < m_2/M_2 < \ldots < m_i/M_i < \ldots m_n/M_n$ or $m_1/M_1 > m_2/M_2 > \ldots > m_i/M_i > \ldots > m_n/M_n$ (depending on whether the results are under- or overrated). It is convenient to plot a graph for drawing a conclusion. This technique can be supplemented, in particular, with the comparison of the sum of quantities of the component being determined based on the analysis of all the separate weighed amounts with the quantity determined by analyzing one weighed amount, the mass of which is equal to the sum of all the individual weighed amounts (balance sample technique, see above). This technique is applicable only if the initial sample is homogeneous enough.

11. Use of Blank Test Data

As it is well known the blank test consists in the carrying out of all the analytical operations under conditions stipulated in the directions, but without the sample of the substance being analyzed, that is the determination of the amount of the sought for component introduced by all the other sources, excepting the sample. The negligible content ascertained in such a manner or a sufficiently exact determination of the result of the blank test (introduction of a correction by subtracting these data from values characterizing the content in the sample) may serve as an indication of the exactitude of the results.

These assumptions are unfortunately not always realized fully. The sources of insufficiently objective conclusions may include: difference in the amounts of impurities introduced in the absence of the analyzed sample and together with it the effect of the sample components on the blank test results; the difficulty of setting a sufficiently stringent experiment involving such operations as, for example, evaporation of diluted solutions to be analyzed, dry combustion of organic substances; impossibility of assessing the impurities introduced at the stages of the preliminary preparation (for example, grinding) and storage of the analytical samples.

12. Use of Data on the Stability of the General Average

In a number of cases the mean value of the content of a given substance in a set of samples is known beforehand (for example, from reliable determinations carried out previously). When a sufficiently large number of current analyses is made the general average of all their results must within certain limits coincide with the known mean. The noncoincidence can serve as an indication of an overall error in all the monitored results. Thus, it is known, that the values of many biochemical parameters of the blood and excretions of the human body of a normal (healthy) human being, and often in pathological cases, obtained in the course of mass analyses, remain sufficiently stable if the averaging is made over a long enough period (day, week, month). A change in such an averaged value is most often the consequence of errors common to the entire set of results and rarely a consequence of the actual change in the contents.[130] The establishment of the real cause, of the two indicated, is the next stage in the proof of the accuracy. As an example we can mention that using such a technique it was possible to establish an error in the determination of potassium in blood plasma and its cause: the low quality of membranes employed in automatic dialyzators.[131]

The efficacy of these techniques is increased when they are used in combination with substances of known composition (RMs, for example) and control charts, as well as in conjunction with a technique known in statistics as the sliding (moving) average. It cannot be excluded that it might prove useful in application to analytical control of some technological processes in which the values of contents are stable, as well as to the control of the state of regional environment.

13. Use of Artificial (Synthetic) Mixtures and Solutions

This technique involves the use of substances simulating the composition of samples and having a reliably determined content value of the component (components) being analyzed. This content is established not through analysis, but through the procedure of preparation. For drawing a conclusion on the accuracy of monitored results, use is made of data from the analysis of such mixtures or solutions carried out according to the method and under conditions stipulated for the determination of the composition of ordinary samples.

Examples of such artificial mixtures are mixtures of the gases prepared under static or dynamic conditions and serving for the monitoring and proving of the accuracy of results obtained by means of gas analyzers. Examples of solutions are those prepared from liquid substances of proper purity and used for proving the accuracy of results of many types of inorganic and, especially, organic analysis. Such solutions can be of the solid type, too, if fusion takes place of known amounts of components without loss. Similar functions can be provided by mixtures of solid substances also, e.g., pure oxides or metals. The sufficiently high reliability of values which are ascribed to the contents of components in such mixtures or solutions is due to the fact that for their preparation use is made only of proven (in the metrological sense) methods of measurement of mass, capacity, pressure, while the determination of composition by analytical methods (this being associated with a high probability of substantial errors) is excluded.

The advantages of this technique include the possibility of proving (monitoring) the accuracy of analysis, with account being taken of the majority of the more substantial errors, that is, the capability of carrying out the overall (thorough) verification; the exclusion of labor-consuming analytical experiment for the purpose of precise determination of the composition of such substances; the possibility of composing from a relatively small set of initial substances different compositions (this is especially important in organic analysis, analysis of gaseous mixtures, etc.); the possibility of effectively applying them directly at the analytical site, including automated analysis, which in many cases is very important.

The most important limitation of the application of artificial mixtures or solutions is due to the fact that it is often difficult to make a full value model of the composition of the analyzed sample (especially when analyzing samples having a complex composition, such as mineral raw materials). Usually an approximation is made, the degree of which should be discussed thoroughly in each case.

If the quality of indicated substances serving as a means of controlling and proving the accuracy of analytical results (as well as calibration means), is certified officially, and they correspond adequately to the analyzed samples, they can be used as RMs.

14. Use of Substances Which Have Been Reliably Analyzed

The utilization of analysis for the determination of the content of components in substances which can be used for proving and controlling accuracy (and calibration), makes it possible to use in principle such substances that are fully identical to the analyzed samples. This removes the limitation in regard to artificial mixtures or solutions while retaining at the same time all the advantages, except for the difficulty of ensuring in a number of cases sufficient reliability of the results of certification of such substances (for example, when determining low contents). In order to solve this problem recourse has to be made to many of the techniques which have been mentioned above. The most proper quality of such substances is attained if they are prepared, studied, and certified as RMs.

15. Use of Substances Simulating the Analytical Signal

For proving the accuracy of results of analyses, use may be made of simulator substances. The best way to illustrate their utilization is to consider an example. Suppose it is required to prove the accuracy of readings of an analyzer used for the measurement of the concentration of boron in an aqueous solution of boric acid. The functional scheme of such an instrument may be based on the measurement of a flux of neutrons scattered in or absorbed by the solution:[132] the intensity of such a flux depends on the content of boron in the solution. The verification can be carried out by using solutions with sufficiently reliable content of boric acid, but for many reasons this is not convenient. In order to eliminate the difficulty we can utilize a solid substance which scatters or absorbs neutrons. For this purpose a calibration graph is plotted beforehand using aqueous solutions. With the aid of the graph it is possible to determine reliably to what concentration of boron corresponds a signal derived from the lump of solid substance — that is, to establish the equivalent concentration. Subsequently this solid substance can be used as a simulator of the analytical signal produced by a solution of corresponding concentration.[133]

The use of simulator substances is expedient when it is difficult or impossible to ensure stability (constant value in time) of the content in substances, for example, moisture in certain materials or hydrogen in many metals.[134,135] For proving and monitoring the accuracy with the aid of such substances it is necessary not only to establish the value of the equivalent content, but also to ensure that it remains constant during the transition from conditions under which it has been ascertained to those under which the given analytical instrument or set-up is used. This method is useful for controlling the instrumental errors and for calibration and instrument verification, but does not account for the errors of the sample preparation, of matrix effect, of method, etc. Besides providing proof and monitoring accuracy, simulator substances can serve for calibration purposes.

A review of techniques employed for proving the accuracy of analytical results shows that only a principle is universal: comparison with the standard containing the component of interest whose content has been established more accurately than that required of the results produced by the analysis technique in question. The individual techniques each have preferable fields of application and specific limitations. Hence, satisfactory solutions can be most often obtained by objective comparison of alternative options, by combination of several techniques and/or in conjunction with an expert consideration of the possible causes of distortion of the accuracy of results.[1,5,7,8,136] The utility of methods of applied mathematical statistics for the solution of these problems is widely recognized. One should keep within view, however, the possibilities and limitations of this or other techniques and use these means appropriately.

IV. SOME PRACTICAL SIGNIFICANT CONSEQUENCES OF ADOPTING A METROLOGICAL CONCEPT

A. Problem of Taking into Account or Disregarding Some Factors

Problems of this kind are quite often encountered in analytical practice. For example: (1) does the presence of some accompanying component affect substantially (or not) the results of determination of the one being detected? What effect has structural peculiarities (e.g., mineralogical structure) of the sample?; (2) has the reagent sufficient selectivity?; (3) can several substances, differing to a certain degree by their composition, be combined for analysis involving a common calibration characteristic, etc.? In all such situations an adequate decision has to be made, i.e., whether it is possible to disregard the effect of one or the other factor which may adversely affect the accuracy of analytical results.

If the influence of some of these factors is strong, then making an adequate decision is not too difficult. On the other hand, when this influence is manifested less definitely, then by applying mathematical statistics a reasonable decision can be made, e.g., an effect is statistically appreciable, but practically insignificant. However, how to define what "practically insignificant" means? Does the analyst always clearly realize the after-effects of making such a decision? Are all of the other parties concerned, e.g., technologist, hygienic specialist, the seller or buyer (user) in agreement with this point of view? And what if not? All the above questions can be answered if a common principle, approved by practice and based on metrological concepts, is used as a guideline.

To illustrate the situation, let us consider the two following examples.

For quite a long time there were discussions on whether the structure of metal alloys affects the results of emission spectrochemical analyses. Then it was shown[2,137,138] that the problem should be separated into two. On the one hand, there is a need to ascertain the tolerable value of error introduced by the "effect" or by its partial exclusion. Let us designate this tolerable value as $\zeta_{\lim}$. On the other hand, the experiment should be planned and realized in such a way that there are grounds to affirm conclusively that when referring to a specific method (for analyses of specific substances), the actual value of the error ζ, due to the effect or its partial exclusion, lies within the limits of $\zeta \leqslant \zeta_{\lim}$. In its turn, the latter is only a certain part of the overall tolerable error $\Delta_{\lim}$ of the results of analysis. So as to establish reliably whether the condition $\zeta \leqslant \zeta_{\lim} < \Delta_{\lim}$ is met with, there should be a definite experiment plan and its proper realization, taking into account all other errors, besides ζ, which by superposition form the overall error of the results of analysis. In other words, the criterion for taking founded decisions on the tolerable value of effects should be based on the value of the overall allowable error and the correct consideration of the correlation between the error introduced by the "effect" and the overall admissible error.

If we are to understand the "effect" not only in its narrow analytical sense (for instance, influence of composition or structure), then we should take into account also the influence of such factors, as the usage of different methods or performance of analyses in different laboratories. As pointed out elsewhere,[7] errors can be introduced even into standardizing documents. Let us assume that we have the average results $\bar{c}_1$ and $\bar{c}_2$ of tests of one and the same specimen (specimens) performed in two laboratories, respectively. There are the known recommendations on product acceptance[139] if $| \bar{c}_1 - \bar{c}_2 | \leqslant \Delta_{\max}$, where $\Delta_{\max} = \sqrt{s_1^2 + s_2^2}$ (the estimates s_1 and s_2 are related to measured values of c_1 and c_2, respectively).

Hence a paradoxical conclusion ensues: so as to facilitate obtaining compatible results there is necessarily no need for decreasing their difference $| \bar{c}_1 - \bar{c}_2 |$, which is both tedious and difficult, but it is sufficient to increase the value of $\Delta_{\max}$, which is easily achieved by increasing the values s_1 and s_2, i.e., by worsening the quality of analyses (!). Thus, the less reliable are the results being compared, then the more there are grounds to consider them as conforming. Actually, in the first place there is a need to specify the permissible value $\Delta_{\max}$ (and similar criteria) and to plan the experiment in such a way so as to make possible the estimation, with sufficient confidence probability, of whether the condition $| \bar{c}_1 - \bar{c}_2 | \leqslant \Delta_{\max,\lim}$ is fulfilled (here $\Delta_{\max,\lim}$ is the allowable value of $\Delta_{\max}$). The delusions, similar to those pointed out, sometimes are encountered in the planning of investigations for producing some RM or in the discussion of the results of said studies.

The conclusions which can be drawn from the above examples may be used in dealing with other similar situations, including those which were mentioned in the beginning of this section. In all such situations, the principal argument should be based not on the opinion used as criterion, but on the tolerable value of the error in the results of analysis. Otherwise, there is a danger of deterioration of the actual reliability of the analytical results, or of the conclusions made on their basis, as compared with the assumed values. This does not imply that the allowable error value should be selected at random.

The respective principles and calculation schemes, including those to be used for determination of values of allowable errors of the results of analysis, are dealt with in detail in papers.[2,7,14,16,25,30,45,46,92,114-121]

B. Optimum Systems of Reference Materials of Mass Application and of Calibration Characteristics

Modern laboratories are quite often concerned with mass control of composition of certain groups of substances, which are to a certain extent similar as objects of analysis. Such are the groups of carbon, low- and medium-alloyed steels, many grades of high-alloy steels, groups of nonferrous alloys, mineral raw materials, soils, etc. Under these conditions a certain optimum strategy seems necessary: if it were possible to provide one certain type of RM for the analyses of a large number of substances, for instance, steels of different grades, this would simplify, speed up, and make cheaper the operation of analytical laboratories. Hence, those responsible for the development of RMs should take this problem into due consideration.

1. RMs for Accuracy Control

It is well known that the methods of chemical analysis are, as a rule, designed to be applied not to a narrow and specific composition of material being analyzed, but to a rather broad one. At the same time analysts would like to have at their disposal RMs, the composition and other features of which are as close to the characteristics of samples to be analyzed, as possible. From the metrological point of view, what does the assumption that a certain RM is "suitable" for the purpose of accuracy control, mean? For instance, suppose a RM in chip form intended for chemical analysis of carbon steel, has according to certificate a carbon content of 0.43%. Is it permissible to use this RM for monitoring analyses of specimens, wherein the content of carbon is 0.5%? The answer is "certainly yes!" And if the content is 0.3%? Yes! Now if the specimens contain 0.1 or 0.8% of carbon? Where is the margin between tolerable and intolerable, and how to establish it? Usually the reply is: "There is no ready answer".

In regard to such situations, it has been reported[2,7] that a RM is suitable for accuracy control of results of analyses of some specimens provided the following condition is met: the error due to the discrepancy between the RM and the specimen is such that the overall error of the results of analyses of specimen remains within tolerable limits. It is open to discussion whether the tolerable value of the overall error has been correctly selected. But once this value has been accepted, the above ratio of errors due to nonideal conformity of RM and specimen, should be maintained. This applies also to errors of determination of contents of elements (compounds) in a RM and errors of ordinary analyses.

The development of the above notions has resulted in the formulation of the concept of the optimum system of reference materials for the accuracy control of analytical results. According to some publications,[2,7,25] the optimum according to metrological criterion system for the accuracy control of analytical results of a certain fixed set of compositions of substances, is such a system which enables the analyst to perform the analysis of all substances, covering all the components to be analyzed, in all their content ranges, with the use of such a number of types (variants) of RMs, which is both necessary and sufficient (but not surplus) to obtain the results of analysis being controlled with such errors which do not surpass the founded tolerable values. Based on this approach to the problem, it seems possible to optimize the planning of systems (sets) of reference materials for the purpose of controlling the accuracy of results of analysis.

2. Calibration Characteristics; RMs for Calibration Purposes

Wide usage of methods based on employment of calibration characteristics, together with the fact that in the above instances one and the same component in different substances is determined with the use of a single and typical technique (e.g., by registering a spectrum) makes the problem of optimizing the sets of calibration characteristics very important. Different variants of calibration are dealt with elsewhere.[5] However, in the present section of this article a different problem is considered. Suppose we have a certain set of substances with a similar, but not identical composition, being analyzed by a method based on the calibration technique (e.g., several dozens of different medium-alloyed grades of steel, all of them containing manganese, which must be analyzed for their manganese content using a spectrometer or a similar instrument for the purpose). Now, what is the adequate number of calibration characteristics (and, hence the number of sets of RMs) which is both necessary and sufficient but not redundant to fulfill the analyses of all the materials pertaining to such a group for a certain component?

As has been pointed out,[2,7,25] this problem, quite in the same way as that of development and use of RMs for accuracy control, should be considered by taking into account, and in this case, even more so, two different and contradictory tendencies. The first one is to combine several substances (or groups of substances) for analyses according to one common calibration characteristic so as to reduce obvious inconveniences due to a multiplicity of characteristics. The second one is to detail the similar dependence with the aim of reducing the errors caused by using less precise characteristics.

Just as in the solution of the problem of taking into account or disregarding some factors, the common drawback which appears when calibration characteristics are being investigated, used, and perfected (a study of interferences from accompanying components, development of techniques for elimination or taking into account interference, elaboration of optimum systems of RMs for calibration, etc.) lies in the neglect of criteria for tolerable error, metrologically well grounded, resulting from the combination of several characteristics into a single common one. The imperfection of such an approach, which was pointed out about three decades earlier,[140] limits to a great extent the usefulness of recommendations formulated on its basis (for a more detailed outlook on normalization of errors with this approach, see Shaevich[141]).

When developing or establishing a set of calibration characteristics which ensure a sufficiently low probability of incorrect results, it is quite important to define the meaning of optimal system of calibration characteristics. The definition[7,25] which follows seems to be sufficiently grounded and acceptable: "such a system (set) of calibration characteristics is considered as optimum for analyzing a certain determined set of composition of substances, which enables the analyst to perform the analyses of all the substances contained in the above set, this with the use of such a number of characteristics which is both necessary and sufficient (but not surplus) to obtain the analytical results with such errors which do not exceed the reasonably founded values".

Based on the above approach it seems feasible to elaborate an optimum planning of systems (sets) of RMs for calibration purposes. The number of types of such reference materials shall, of course, depend also on the range of content, covered by one or the other calibration characteristic.

C. Quality of Reference Materials

Above we have viewed the consequences pertaining to the usage of RMs. Now it seems essential to discuss the effects of RM quality, this as an integral part of the analytical process. Once again we have to deal with tolerable errors due to such factors as nonideal homogeneity of RMs and quality of experiment carried out to determine the values of quantities (contents) to be indicated in the certificate, and possible lack of stability of contents in time. We should also look into the criteria for judging the interchangeability of two or more types of RMs (e.g., of the first or subsequent issues, or these supplied by different manufacturers).

In general, this part of the problem does not apparently present such wide interest as the preceding ones, since each analyst is certain that the quality of the RM is guaranteed by the manufacturer. The latter, in all probability, are aware of the responsibility that is imposed upon them. However, as experience has proved, there is always the possibility, as termed by the legal mind, of unintentional error. Therefore, below is given a summary of the more principal consequences of adoption of metrological concepts, which is valid for the described situation. Generally speaking, this part of the problem deserves to be dealt with in a separate review.

RMs, when viewed from metrological positions, should be regarded as a variety of metrological means, i.e., measures which serve the purpose of storing and reproducing the values of quantities characteristic of the chemical composition of substances (content or mass of certain components). Such an approach to the problem has passed the evolutionary stage from being merely discussional to the one which is sufficiently recognized. The vital consequence of the above lies in the fact that the characteristic values pertaining to the quality of RMs, acting as measures, should be designated and realized with account taken of the tolerable errors of the results of the analyses which are catered to by the respective RMs.

True enough, at present there prevails an opinion that RMs are not, strictly speaking, measures as defined in classical metrological science. Some metrologists regard the RMs as an "enfant terrible". On the other hand, there are others who view the RMs as a product of manufacture, principally not to be distinguished from any other product the quality of which is guaranteed by its manufacturer (seller). But such an approach fails to take into account the metrological aspect of the problem, which cannot be discarded. Commercial weights are also articles of mass production, but their manufacture entails certain restrictions regarding the limits of tolerable weighing errors.

For more detailed information on the correlation between RMs and classical measurement means, see Section VI.

As a general rule, the manufacturer of RMs should ensure that the error Δ^{RM}, necessarily introduced as a result of nonideal quality of RMs into the results of analyses, does not substantially raise the tolerable overall error Δ_{lim} of the result of analysis:[2,141]

$$\Delta_{RM} \leq \left(\frac{1}{k}\right) \Delta_{lim} \tag{4}$$

The value of k may be substantiated by taking into account a number of circumstances, such as whether the RM is intended for independent application or for use in a set of RMs, how important is the purpose of field analyses performed, etc. Usually $2 < k < 3$. But from this simple expression quite serious consequences ensue, as far as the manufacturer of the RMs is concerned.

It is known that:

$$\Delta_{RM} = f(\epsilon_1, \epsilon_2, \epsilon_3) \tag{5}$$

where the errors ϵ_1 are introduced as a result of residual inhomogeneity of the RMs, ϵ_2 the errors due to nonideal quality of certification analyses or procedures of similar purpose, ϵ_3 are the errors caused by the instability of RM composition in time. Noteworthy is that Δ_{RM} value cannot always be expressed in terms of the square root of the sum $\epsilon_1^2 + \epsilon_2^2 + \epsilon_3^2$.

Now we have approached the more difficult part of the problem. If Δ_{lim} in the formula (Equation 4) is equal, for example, to 6% (relative), then one must ensure that $\Delta_{RM} \leq 2\%$ (relative) with $k = 3$, or that $\Delta_{RM} \leq 3\%$ with $k = 2$. Hence, there is a need to distribute these 2% or 3% among the values of ϵ_1, ϵ_2 and ϵ_3. Let us assume, for the sake of simplicity, that $\epsilon_1 \approx \epsilon_2 \approx \epsilon_3$ and that $\Delta_{RM} = \sqrt{\epsilon_1^2 + \epsilon_2^2 + \epsilon_3^2}$, then we should have: $\epsilon_i \leq 1.1\%$ (with $k = 3$) or $\epsilon_i \leq 1.7$ (with $k = 2$). This is difficult to realize (e.g., to ensure that the inhomogeneity lies within such small limits). It is still more difficult to make sure that this condition is met, since it is necessary to establish with great reliability the fact that the errors do not exceed very minute values.

A more detailed examination of this aspect of the problem (including the determination of optimum levels for tolerable RM errors, the peculiarities of planning experimental work for monitoring material inhomogeneity within very small tolerable limits, carrying out of certification analyses, evaluating the stability of material composition in time, and comparing RMs of different issues) is a separate subject.

V. METROLOGICAL ASPECTS OF MANAGEMENT OF QUALITY OF ANALYSIS

A. Data Analysis and Decision Making

The analysis of data characterizing the operational quality of a laboratory or another section of the analytical service is required for monitoring the said situation and, if need be, for developing a program of improving its functioning. To a certain extent, data analysis is performed in the course of current or consecutive control of results of laboratory work. However, the wording data analysis is more often related to the process of obtaining and discussing the generalized conclusions, and moreover, to establishing some relatively more common regularities.

Data analysis may be undertaken prior to the initiation of accuracy and precision monitoring (including statistical control), in the process of establishing of this control and thereafter. In the first case, the analyses may yield the needed information, e.g., about the initial level of accuracy and precision; in the second case, about the improvements in the system, as to the effectiveness of monitoring and control, as it is enhanced, and finally, as how to maintain the achieved control level.

As is known, the control functions are rendered difficult in case of both insufficient and excessive information. Hence, the importance of determining, in regard to each section of the analytical service, the optimum list and the amount of data which are both necessary and sufficient (but not surplus) to give grounds for making decisions. In such cases there is a need for carrying out a study of the general informational structure of the object of control, at first from the qualitative point of view (enabling the analyst to characterize the task being considered and to point out the essential factors) and then proceed with the quantitative solutions. As experience shows, the following objective information is both necessary and sufficient: (1) on closeness of results of parallel-conducted measurements (this, if the result is obtained as a sum of two or more of such determinations) which is achievable by elementary processing of such data (or, in the simpler case, by comparing the data); (2) on the stability of results of analysis (in the general case — averaged results based on the data of parallel-conducted measurements) for which it is sufficient to repeat the analyses of an identical sample (still better a blank sample) and not necessarily a costly RM; and (3) on the magnitude of bias of the entire group (set) of results relative to the actual values of contents, for which purpose RMs or other analogous means must be used. The error of each of the separate analytical results may, in principle, be attributable to each one of the above-mentioned causes. Therefore, all of them should become the objects of data analysis and serve as bases for elaboration of management decisions.

In connection with the problem of data analysis, it seems logical to consider two other circumstances: first, relevant to the situation which should call for an interlaboratory experiment as a source of information, and second, regarding the degree of accuracy ensured through the use of RMs and similar means and techniques.

Interlaboratory experiments, as the means used for judging about the reliability of field analyses data, are quite widely popularized and, in many instances, there are sufficient grounds for doing so. On the other hand, it can be shown that such an experiment is not always necessary and when so, they can be regarded only as auxiliary means of comparative assessment.

Suppose there are two laboratories (the manufacturer's and the consumer's) which are analyzing quite the same samples. In each of the laboratories the analytical process is statistically controllable, while the accuracy of results is monitored through the use of the same RMs. Furthermore, let us assume as established the fact that the average deviation of results of field analyses from the actual values of content in the samples being analyzed in each of said laboratories does not exceed $\Delta_{\lim}$ (for the accepted confidence probability), which is in agreement with the relevant requirements. In such a situation it can be assumed that the error $\Delta^{x}_{i} - {}^{x}_{i}$ of comparison of each pair of results obtained in different laboratories does not exceed $\Delta_{\lim} \sqrt{2}$, being the error of the difference of the two values. And as long as the initial assumptions remain true (which fact can be ascertained when there is an effective system of assuring the precision and accuracy in both laboratories), there seems to be no need to proceed with a special interlaboratory experiment: the possible discrepancies may be calculated considering that $\Delta^{x}_{i} - {}^{x}_{i} \leq \Delta_{\lim} \sqrt{2}$. All the aforesaid can be confirmed by means of a trivial example: if a check and adjustment of each of a number of clocks is achieved by means of a "true time" signal, then there evidently is no need to check the readings of one clock vs. the readings of another. In such cases, however, when the analytical process is insufficiently controllable, then the interlaboratory experiment (and the like) should be considered both as important and useful means for obtaining relevant information required for performing data analysis and making decisions.

This can be confirmed by the fact that interlaboratory experiments in regard to the tasks of field analyses, are, as a rule, not practiced in the branches of industry characterized by sufficiently low errors of analytical results (this mainly due to the combination of favorable conditions, such as: traditional objects of analysis, correct and adequate methods used, qualified personnel, availability and systematic use of RMs), e.g., in ferrous metallurgy. On the other hand, when such conditions are absent (e.g., when analyzing new kinds and types of products, manufactured by the chemical, pulp-and-paper industries, when performing clinicochemical analyses, monitoring over the environmental pollution), the interlaboratory experiments are carried out more often (although not always as often as they should be).

The interlaboratory experiment is quite a valuable means, in itself, also when inspectional control is enacted, or when the state of measurements is being checked, etc.

The second point, which we consider as important, is the taking into account the errors which are associated with the use of RMs. As is known, the completeness of exclusion of such errors will depend, to a great extent, on the quality of the RMs and on mutual correspondence between the RM and the specimen, i.e., in analytical sense, such as common composition, presence of bothering admixtures, etc. When speaking about the error characterizing a RM, the best situation will be such when the error is negligible, which, as a rule, is achievable. Now, when we are dealing with errors caused by incomplete correspondence of the RMs and the specimens, then the situation looks much more gloomy. The detection and quantitative evaluation of such errors is actually quite a difficult task. This problem can be solved if information is available about the reliably established quantitative indices of the influence of some factors (e.g., different content of accompanying components in a compound) on the accuracy of results of analyses. Insufficient certainty of such information may leave undetected some of the more substantial errors. This concerns not only the RMs but also all the other means and methods of accuracy control and calibration monitoring.

All this shows that the analysis of data and elaboration of decisions to be taken on the monitoring of the quality of analyses cannot be reduced to a certain formalistic approach. In each particular case there are the following decisions to be made: which kinds of analyses should be controlled in the first place; how the control should be effected; what criteria should be used to judge the situation (or the state of affairs); what should be done to correct an inadmissible situation. All this calls for using a combination of methods for obtaining unbiased information, (including, and sometimes essentially, mathematical-statistical presentations and calculation methods), with a profound professional knowledge in the sphere of quantitative analysis and neighboring subjects, besides.

B. Certification of Methods

The standardization of analytical methods has gained sufficiently wide recognition. However, its positive effect, as a means for selection on the best variants of methods and their legitimization in norms, is, to all regrets, limited for a number of reasons. The standardization of methods, not only at the international and the national levels, but also at the levels of the industrial branch, amalgamated enterprise, works, etc., as a rule, lags behind the up-to-date needs. Besides, the diversity of substances being analyzed, instrumentation used, and the conditions under which analyses are made, also the requirements to be met, is so great that it is usually impossible to pack all this information into the text of even a high-class standard (e.g., a state standard). There is also the taking into account of the intensive updating of technological and ecological processes which are subject to monitoring, also renovation of analytical instrumentation and techniques. As a result, the standards of relatively high categories mainly relate only to the techniques of analyses of raw materials and ready products, and even then do not cover all of them, often lagging behind time, without effectively reflecting all the important changes in the technical situation. And, finally, it is inexpedient to standardize many of the methods (e.g., owing to a limited number of manufacturers and consumers).

Some of the circumstances pointed out are quite typical also in the case of the measurements of other variables, besides the value of contents. Owing to that, gaining recognition now is the concept of metrological certification of nonstandardized techniques of measurements. The essence of this concept consists in that a procedure is implemented with the purpose of confirming and officially substantiating the usability of a certain method for solving one or the other metrological (in our case analytical) problem. There can be two approaches to realize this concept: the first is to implement a procedure which has the purpose of only establishing the metrological characteristics of the technique being certified under specific conditions of its application. The choice of an appropriate technique from a number of certified methods is in the hands of the analyst. The second approach, in line with the realization of the above-mentioned purpose, consists in establishing what substances (or groups of substances) shall be officially covered by the said technique. The choice between one or the other approach to this problem shall depend on specific conditions.

The similitude and difference in certification and standardization of analytical methods are given consideration elsewhere.[7] It is shown that there are no differences, as to the purpose, viz., in both cases there exists a need to assure a certain level of accuracy and precision (sometimes also — speed or efficiency). As to the method of fulfillment, standardization features, in general, a more profound way of treatment of the aforementioned problem (comparison of different variants of the technique, a preliminary check-up of the variant—assessed optimally in a number of laboratories, taking into account the interests of the parties concerned, especially the consumer's, which is compulsory). There should be no substantial differences from the method, logically. In both cases the purpose of the method must be specified, the procedure of analysis and treatment of results must be described, the means and the order of monitoring the accuracy and precision must be specified, the respective norms should be elaborated and described, and finally a check should be made as to whether all the information contained in the standard or certificate can be realized in practice. The differences as to the criteria of choice (between certification and standardization) are quite substantial. The criteria for standardization are well known, while as regards certification it is justifiable to certify those techniques used (or their variants), which have not as yet become standards, or such methods, the standardization of which would be a long-term procedure, and those the standardization of which is deemed unnecessary.

The process of certification should have its documentary result in the form of a certificate on the given technique. The widespread drawback of certificates, as well as quite a number of standards, is the lack of certain important specifications. Thus, the errors are often specified only in the form of tolerable discrepancies between the results of parallel measurements, which fact, as is well known, leaves the accuracy of obtained results without the scope of control. This is sometimes excused by the margin of quality of substances being analyzed (as to composition), by the less important application of the given type of analyses, lack of means for monitoring the accuracy of analytical data, and, in some cases, even by the belief that if the analysis has been performed in strict compliance with the specifications of the technique, then the result obtained must be correct. Such explanations, however, cannot be regarded as justification of incompleteness of norms or specifications. The accuracy control is needed in principle (although the requirements in regard to accuracy may be quite different), while various means for achieving accuracy can be employed, even if their efficiency is far from ideal. Such assertions, that if the analysis is fulfilled in strict compliance with the specifications, then the result should be *a priori* correct, are mildly speaking only a delusion. Besides the usage of norms, quite desirable are the stipulations regarding the means, methods, sequence of operations, and the time schedule of monitoring of accuracy and precision of analytical data. All the potentially significant errors should, as a rule, be monitored. The techniques used for monitoring should be correct from the methodological point of view, sufficiently simple, economical, and clearly specified. The same is quite true regarding the specifications covering the order of monitoring and its time schedule. Hence, to be avoided are such instructions as: "for accuracy control use should be made of an appropriate RM", since it is more correct to specify a definite type (or composition) of RM to be used. As to the means of accuracy control of the results of analysis, only such that are readily available for the use of those who will be working with the certified technique should be specified.

When regarding the certification in general, it seems important to underline that elaboration and objective assessment of requirements, substantial foundation of the possibility of their realization, and a number of other steps in regard to a critical and systematical consideration of the situation should precede the official establishment of the analytical procedure and the control of the results of analyses.

C. Accreditation of Laboratories

In the last few years increased recognition has been given to the official accreditation of laboratories.[142-163]

Among the principal factors determining the quality of laborabory work are the following: the level of management, the means available in the laboratory (its equipment), qualification of personnel, availability of an effective system of control (assurance, proof) of the quality of analyses fulfilled. Thus, one of the suggested recommendations[142] points to the need for obtaining and analyzing three different groups of data. The first of these pertains to provision of metrological assurance including the data on calibration programs; standardization of test techniques and measurements; on terminology used; on the links of the physical means used, and the numerical data with the means and data of a higher level; on the reliability of such means and data; and on the registration, processing, and transmission of results. The second group is related to the control of the quality of tests and includes the data on reference samples, techniques of analyzing the data, registration of detected discrepancies and on the programs of specimens exchange with other organizations. The third group of data pertains to the assurance of quality of tests and includes the data on representativeness of specimens, the frequency of periodical inspections, their thoroughness, and completeness of information obtained as a result of inspections. The approach reported[151] makes allowance for the following to be taken into account when accreditation is implemented: complete abidance by the norms (specifications) of technical documents; availability of the requisite measurement means and proper conditions for their operation including documents specifying the operation of laboratories; requirements in regard to adequate qualification of personnel, proper facilities, and operating conditions. If necessary, there should be a system of checking the results of analyses and their correctness through the use of blind control specimens; also the data on previously made checks and inspections, as well as the data on submitted claims, should be used upon the completion of accreditation procedure; the periodical supervision on the part of metrological authorities concerned should be welcome.

When such recommendations are being considered, it is regrettable that they fail to give grounds for the assumption that methodological concepts pertaining to the evaluation of the quality of operation of laboratories, including their accreditation are well founded. To a certain extent this can be explained by the complexity of the problem in general and by the presence of a number of specific, particular, side problems, which need to be solved. The importance of a systems approach to be used from the methodological point of view in search of a most efficient solution of the problem has been pointed out, and below are reviewed the basic concepts[7] formulated on the basis of such an approach.

From the position of a systems approach, the aim of a laboratory (or a section of "instrumental" control) is the assurance of the consumers with proper results of analyses, i.e., the product of the laboratory. This is well known and brings about no objections. However, as soon as in compliance with the methodology of systems analysis, there is an attempt made to judge the criteria (parameters) to be used for evaluation of the quality of laboratory performance (or section of control), the possibilities of "obvious" solutions are quickly exhausted. This can be shown by formulation of several of the more substantial questions.

Is it sufficiently well founded to evaluate the condition of a laboratory (for the purpose of its accreditation) only on the basis of the presence of requisite facilities (laboratory equipment, its quality and condition, qualification of personnel, availability of norms and standards, control system, etc.), or the final results should be taken into account, as to the laboratory functioning (e.g., of results of analyses which have arrived behind scheduled time, or were found to be erroneous)? Is it possible to evaluate the quality of laboratory operation under general conditions when it is not determined by one single parameter, but by several, and when, as a rule, not one single analysis, but a multiple of different kinds of analyses are performed, each of them in different numbers or of various importance? Can such generalized evaluations be considered as objective and do they stimulate the improvement of the performance of laboratories? And finally, what is the scheme of action in such a complicated situation?

In trying to find the most substantiated replies to such questions, it should be stressed that the presence of prerequisites, as pointed out above, in all reality increases the probability of high level performance of laboratories. Therefore, during the accreditation it shall be necessary to check whether such prerequisites are available. However, it would be incorrect to limit one's actions to this check. The most important criterion is the final result of activity of a laboratory. If all the required measurements are duly fulfilled, with the duration of analyses not exceeding the preset values (and efficiency not lower than prescribed), and, with sufficient reliability of results, while such a state of affairs is confirmed by objective data, then this should be considered as a decisive argument in favor of accreditation of the laboratory.

However, it is not at all simple to assure an objective analysis of the quality of laboratory performance for quite a number of reasons. Not one single criterion but several should be used, while the multitude of the analytical tasks catered by the laboratory should be taken into account. Besides, the consequences of different shortcomings in the activity of a laboratory are not the same. Owing to this it is important to discuss in detail the methodological aspects of the solution of the problem of laboratory accreditation.

In the general case, the current activity of a laboratory can be represented as the operation of a set of elementary sections (as a kind of a multidimensional matrix):

substance being analyzed	$S_1, S_2, \ldots S_i, \ldots S_n$
component being determined	$K_1, K_2, \ldots K_i, \ldots K_n$
range of contents of component being determined	$D_1, D_2, \ldots, D_i \ldots, D_n$
technique	$M_1, M_2, \ldots, M_i, \ldots, M_n$
analyst (instrument)	$A_1, A_2, \ldots, A_i, \ldots, A_n$

Each elementary section L_i (including the members S_i, K_i, D_i, M_i, and A_i) of those required, for example, for monitoring a certain technological process and the quality of manufactured product should be active and yield the results of analyses with a requisite reliability and speed (or efficiency).

Let us consider at first a more simple variant of accreditation, when only one active section is functioning within the laboratory constitution, i.e., L_i. If the operation of this section is in compliance with all the requirements, then this section can be accredited. But if even one of the requirements is not met with, then what? At first there is need to elucidate what is meant by "in compliance with the requirements". Continuing this discussion in regard to a certain singular requirement, e.g., the requirement of accuracy, we can assume that the results of all analyses performed by this section are incorrect. In the latter case, evidently, there are full grounds to withhold the accreditation. On the other hand, if the percentage of erroneous results is only 1.5% or 10%, what then? Hence the need to determine the acceptable percentage of such results. This calls for objectively taking into account the consequences (technical and economic or other, e.g., connected with the assurance of trouble-free operation of a technological unit). As a result, a certain criterion should be elaborated: if the actual percentage of erroneous results does not exceed an objectively tolerable value k, then there are grounds for accreditation of section L_i according to the given parameter (reliability).

In the general case, if we take the number of such basic requirements to be m, then the condition for the accreditation of the given section is that each of the following inequalities shall hold:

$$\begin{aligned} k_{1.1} &\leq k^*_{1.1} \\ k_{1.2} &\leq k^*_{1.2} \\ &\cdots\cdots\cdots \\ k_{1.m} &\leq k^*_{1.m} \end{aligned} \tag{6}$$

(the first index in each pair pertains to the section, while the second pertains to the requirement).

In case of a laboratory, i.e., a system comprising n elementary sections, the condition for accreditation is that the following inequalities shall be satisfied:

$$\begin{aligned} k_{i.1} &\leq k^*_{i.1} \\ k_{i.2} &\leq k^*_{i.2} \\ &\cdots\cdots\cdots \\ k_{i.m} &\leq k^*_{i.m} \end{aligned} \tag{6a}$$

Here the value of each of the criteria: $K_{i.1}, K_{i.2}, \ldots, K_i$ for all the values of $i = 1, 2, \ldots, n$, e.g., for each of the section L_i (see above) should be objectively founded, and not in general, but taking into consideration the importance of each kind of analysis. In order to assure sufficient objectivity it is necessary, as pointed out earlier, to take into account comprehensively all the consequences of a situation. Based on experience gained in the standardization field, an important condition for this is the joint work of both the manufacturers and the users of the given product. The same principle can be successfully realized in the course of accreditation of laboratories.

Thus, the accreditation of laboratories should be considered as a multiparametrical and multicriterial problem. When solving such problems, in regard to the quality of products, sometimes it is deemed appropriate to introduce a certain generalizing criterion (qualimetric evaluation). In the case being considered, when we are concerned about the quality of performance, the elaboration of such a criterion and its unification regarding the peculiarities of operation of different laboratories is to be considered as a necessary, but also a complicated problem. The principal difficulty seems to be not in compiling a list of particular indices (parameters) in regard to each kind of analysis, but in the fact that such lists will be varying in different laboratories, and also in that the "weight" for each particular parameter is assigned by human beings, hence shall be inevitably differing in various laboratories. Such unification is not simple. We cannot discard, as well, the difficulties caused by the fact that the low values of one parameter, brought about by the unfulfillment of one certain requirement (e.g., speed), may be compensated by a high value of another parameter characterizing another requirement (e.g., accuracy); poor functioning of one certain section may be masked by the proper operation of other sections, etc.

To summarize, it can be asserted that an objective accreditation of a laboratory is possible only when the following three principal conditions, as a minimum, are fulfilled: (1) there should be objective (and not random, episodically provided) information on the real value of each of the parameters characterizing the operation of each section; (2) there should be, for every specific situation, a justifiably defined permissible percentage of results of each kind of analysis (from among those actually performed in the laboratory) which are not complying with each of the stipulated requirements (including reliability); (3) there must be elaborated and officially established a certain approach to be agreed upon by all the interested parties, determining the order of working out a resolution on the quality of laboratory operation, in general, taking into account the prerequisites for high quality performance and the actual results obtained.

If the above conditions are not complied with, then the effectiveness of the preliminary work preceding accreditation, the accreditation itself, and the subsequent inspectional supervision will be substantially of lesser value.

VI. SOME THEORETICAL PROBLEMS; PRACTICAL CONSEQUENCES

There is the well known saying: "Nothing is more practical than a good theory". Taking heed of this, there is reason to consider the theoretical aspects of the metrological assurance of quantitative analysis.

As is well known, the classical metrological approach consists in elaboration and realization of the so-called, hierarchical verification chains, i.e., methods of transmission of the value (size, or dimension) of a certain quantity from a standard of unity onto the level whereon the field measurements are made.[50] The proposed concept of traceability[164,165] does not introduce any principal changes into the above-mentioned approach, since it also implies the necessity to establish relationships between working measurements and the reference means. Reports as to the advisability of such an approach in regard to quantitative analysis have appeared beginning from the end of forties,[40,42,43] while the elaboration of respective models dates back to the mid-fifties.[2,3,7,10,13,15,22,122,167-171] By the present time some experience has been accumulated in the realization of such an approach (see below). At the same *time, there are publications which are concerned with the use of nonstandard methods,* and also the papers which advance a thesis that the measurements based on the standards of basic physical unities and on standard reference materials form two independent systems.[172] In the quest of a roundabout way to obviate the difficulties connected with the assurance of the entire set of analyses with RMs, hopes are pinned to the absolute methods. Hence, the need to discuss the situation.

A. Nonstandard and Absolute Methods

1. Nonstandard Methods

Now and again there are reports appearing concerned with the development and the advantages of the so-called nonstandard methods of analysis (spectrochemical, mass spectrometric, isotope dilution, and others). However, if the quantitative analysis, in regard to its general purpose, is a measurement process, then the existence and effectiveness of the nonstandard methods can signify only one of the two facts: either the failure of the basic metrological concept — that every measurement, in the final count, is reduced to the comparison with a measure, or that the above-mentioned methods are not nonstandard in the metrological meaning of the term.

Dealing with this problem it has been shown[173] that even in a relatively simple situation, i.e., that of determination of an element in its compound solution, e.g., with the use of the *coulometric method, there are no grounds to call it a nonstandard method.* The weights, volumetric glassware, and electrical measuring instruments used in this instance, are actually measures, i.e., the parts of the hierarchical systems of similar means, at the summits of which there are the standards of units. Quite often under such circumstances (e.g., for a titrimetric analysis) there is need for reference substances, for example fixanals, which are also traceable to respective basic measurement means. In more complicated cases there is need not only for classical measurement means (for mass, capacity, electrical, and optical quantities, etc.), but also for specific substances — carriers of the content of component being determined in some substance.

Such circumstances are often overlooked. Thus, in relation to an activation analysis with the use of substoichiometric method,[174] two variants are discerned, one termed as relative (standard) method and the other with variable number of carriers (nonstandard) method. In the first case the content of an element is calculated by comparing the activity of specimens with the reference substance after dissolving and adding equal and precisely known amounts of carrier. In the second, the irradiated specimen is divided into two equal parts, then in adding to one of the parts an aliquot of a known amount of carrier, a substoichiometric separation of same amounts of the element being determined is ensured and, finally, the activity of the thus separated specimens is measured and the unknown content is determined by calculation.

Not denying the advantages of the second variant, it should, however, be pointed out that *the function of "transfer" of the values of quantities characterizing the content,* is likewise realized in this instance: use is made of sufficiently precisely known amounts (mass) of a substance-carrier. It is expected that during the substoichiometric separation (e.g., with the use of radiometric titration) a determined amount (mass) of used reagent shall correspond to a determined amount of unknown (being determined) component, not to mention the use of such metrological means, as weights, burettes, etc., each of which, as is well known, is traceable to a respective standard of a unity. Besides, as a common feature, in our case there still remains the problem of numerous sources of inaccuracies.[175,176] This renders highly expedient the use of the accuracy control means, i.e., the RMs and other substances of similar purpose, which, in fact, are metrological means.[2,3,22,40,50,177,178]

Hence, taking into account all the situations, as described above, there are more grounds to speak of not nonstandard methods, but more righteously to refer to methods which do not require (or require only rarely) the direct use of reference materials or means of similar purpose, in each particular case of field analyses. This is also true in respect to nonstandard techniques based on calibration principle. The fallacy of such an approach is demonstrated elsewhere.[179]

It is quite possible that such a situation can be attributed to the closeness of terminological expressions standard of a unity and SRM (standard reference material). So as to avoid possible misunderstanding and to enhance methodological stringency, we consider it advisable to propose for such methods a special term, discarding the so-called technicality term.

2. *Absolute Methods*

The absolute methods are defined as those in which the measurement value of a quantity is determined directly in the base units of measurement, or based on the relation of the said quantity to the measurement units through the use of fundamental equations.[22,122] Such methods find their application or are suggested for use in different variants of coulonometric determination of elements, e.g., metals in solutions, or cryometric determination of the purity of organic substances, spectroscopic nonelastic electron scattering method for the determination of fine film composition, etc. It would be wrong to dispute some of the obvious advantages of such methods, but on the other hand, there is a number of limitations which should be taken into account.

As has been said earlier (see Section I.B.), in the general case quantitative analysis procedure includes not only the measurement of a separated analytical signal, but also the preliminary steps, i.e., opening up of the samples, separation and concentration of the components, etc. Due to this, even with the use of the absolute method of measurement of the separated analytical signal, there will always be doubt as to whether the above method will suffice to yield a correct result. This is explainable by the fact that there is always the possibility of errors (usually predominating), which originate, as a rule, at the preliminary stages of the analytical procedure. Therefore, the use of the absolute methods will be effective only in regard to such substances, the analysis of which does not require any preliminaries, i.e., the operations described above, or when there are sufficient, critically evaluated grounds for deciding that such operations are not liable to introduce any substantial errors. Among the substances the analysis of which by absolute methods shows promise are the following: mixtures of gases, certain solutions, also certain complex solid substances, provided that under all such circumstances the components (including all possible admixtures) do not distort the working analytical signal or the respective distortions are assessed duly. The absence of distortions and full allowance for the sources of errors should be provided with such strictness, which is necessitated by the purpose of the given type of analysis (see Section IV.A.). Of course, such rigorous proof is required for the elaboration and use of any methods in regard to any definite substances and not necessarily only of the absolute methods. However, the extensive promises attributable to the latter, and considering the danger of noncritical overestimation of such methods, make it necessary to attract attention to this point.

It is also quite natural that the absolute methods cannot be regarded as nonstandard ones. Moreover, the linkage of such methods with the system of reproduction, storage, and transmission of values (sizes) of basic measurement units is manifested in a particularly distinct manner.

B. Peculiarities of Hierarchical Transmission of Measurement Information Regarding Quantitative Analysis

Basically the term measurement information is understood to mean the information relative to the values of physical quantities being measured. When we are dealing with quantitative analysis there is obviously the need for measuring many of such variables, but the final goal consists in measurement of a definite component. More often it is expressed in the form of a ratio of the mass of said component to the total mass of the substance. However, although the problem in the final count amounts to the measurement of the ratio of masses, it cannot be solved only through the use of means devised only for mass measurements. The reasons for this, as pointed out earlier, (see Section I.B.) lie in the nature of chemical analysis: the need for separation through the use of specific means and techniques (which are usually different for diverse groups of substances and components being determined), of a working analytical signal, under conditions wherein specific sources of error may be active. The analysts, regrettably, as a rule do not possess the means to calculate readily and accurately the numbers of particles of the component being determined (atoms, ions, molecules, functional groups) and the particles of other components contained in the specimen, with the aim of determining the unknown quantity, i.e., the content in terms of ratio of masses (weights) by using the data on atomic (molecular, etc.) masses (weights).

The above-mentioned obstacles leave out the possibility of a direct inclusion of chemical composition measurement into the system of reproduction and transmission of sizes of units of mass and compel the scientist to elaborate a specific system relative to the quantities characteristic of the content of elements (compounds). It is evident, beforehand, that the above system should be linked with systems pertaining to the basic units of physical quantities. It is also obvious that such a system should be based on proven general principles, and also should take into account the peculiarities of the problem, such as the presence of operations difficult to control, but which are necessary for the separation of the working analytical signal (opening up of sample, separation, and concentration of components, etc.), diversity of substances being analyzed and of components to be determined, variety of ranges of contents of the latter and of admixtures, as well as the multiformity of the physical and chemical principles on which the working (field) methods of analyses are based.

The majority of analysts and metrologists acknowledge the fact that the standards of the basic physical quantities, the methods of analysis, reference materials and other similar means are linked in a certain way. There have been reported different variants of respective schemes.[3,4,13,22,40,43,122,166,168-170]

It seems important to develop further such schemes and concepts and then take the next step — to consider further possibilities, limitations, and experience gained in their realization in regard to the analyses of certain groups of substances. To settle this problem it is expedient to begin the consideration on the lower level, i.e., of performing field analyses.

1. General Scheme of Linkage Between Field Methods of Analyses and Metrological Means[7,169]

In general, quantitative analysis consists, as pointed out earlier, of several stages. Thus, during the process of analyzing solid inorganic substances by the gravimetric method, a weighed-out portion of material is taken, dissolved, the elements are separated with the aim of isolating the element to be determined, the mass of the separated compound of the element analyzed is determined and finally the calculations are made. As shown in Figure 11 relative to the field analyses, the above-mentioned stages are designated as: a_1, b_1, ..., i_1 ..., n_1. In its turn each stage may consist of more simple processes: i_1a_2, i_1b_2, ... i_1i_2, ..., i_1n_2 (the first index in each pair pertains to the level characteristic of the more complicated processes, while the second, to the level characterizing the constituent for the given stage, less complicated processes). A further detailing is possible, taking into account still more simple measuring processes, e.g., $i_1i_2a_3$, $i_1i_2b_3$, ..., $i_1i_2i_3$, ..., $i_1i_2n_3$ (the principle of indexing is quite the same), until the k-th level. It is only natural that under specific conditions some of the constituents may be missing.

The metrological assurance of a part of such measurement processes is catered to by the traditional methods. Thus, the accuracy of readings of balances is ensured by their adjustment

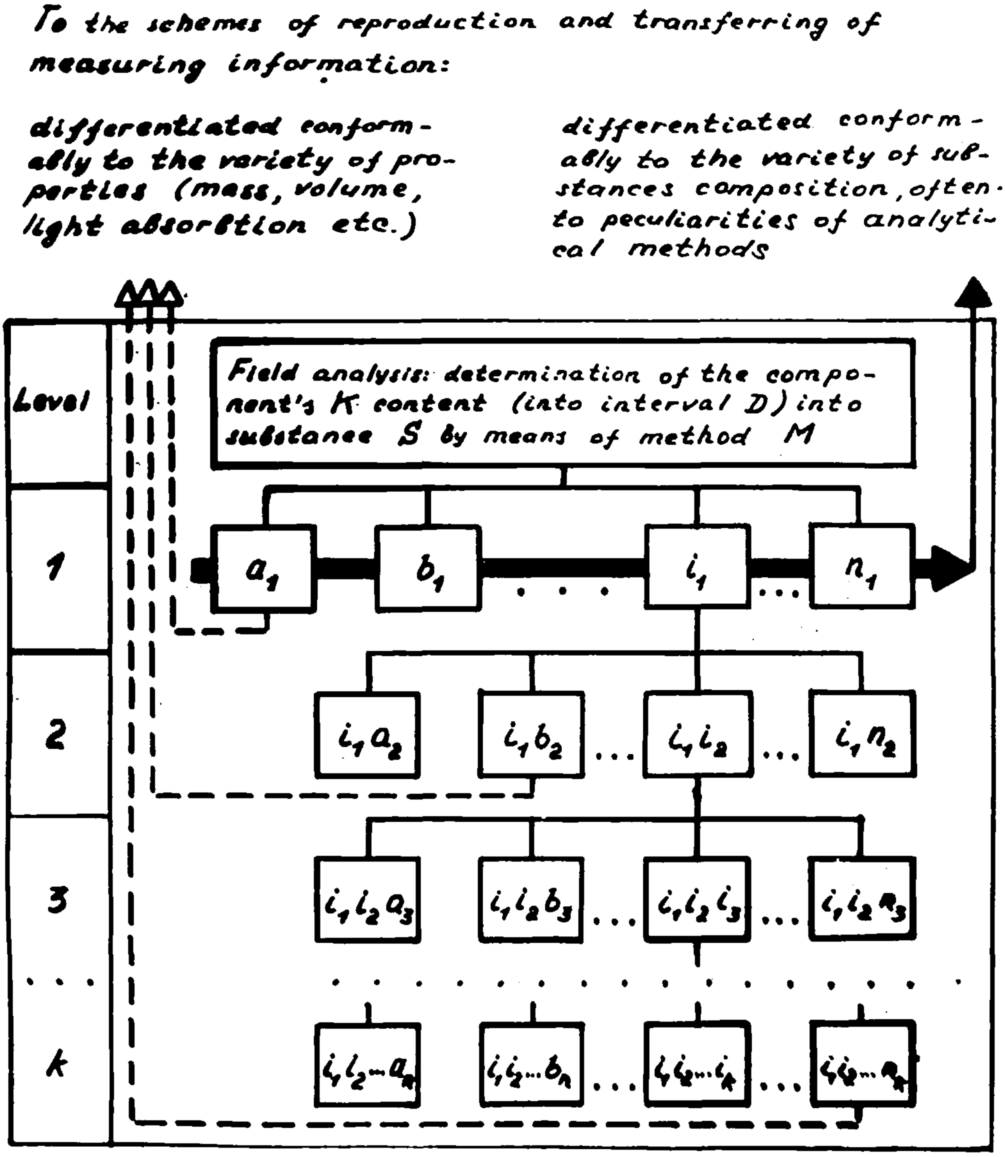

FIGURE 11. Block diagram of quantative analysis procedure and its relationships with means for Unit-by-Unit and overall (thorough) verification and calibration.

and periodical checking with the use of means, acting as linkage in the verification scheme for mass measurements. The same applies, for example, to the instruments used in electric or optical measurements. According to this, the structure of the subsystem being considered, calls for acquisition of measurement information with the help of means included into the verification schemes, differentiated as to the kinds of quantities being measured, and not as to the substances which must be analyzed. Such schemes are intended for the so-called "block" verification (structural elemental or unit-by-unit checking) or calibration. (Note: here and in similar situations, considered are, of course, the structural elements of the schemes and not the chemical elements; the difference will be clear from the context). It is to be noted that these schemes, regarding the problems of quantitative analysis, can include as reference means not only methods and instrumentation, but also substances, for instance, the so-called primary standards for different variants of titrimetric procedure. Such substances, should be justly called reference materials for block (elemental) verification or elemental calibration, if they are being used for the latter purpose. The selection of such a group of substances and the introduction of a respective term reflect the fact that the verification or calibration is performed in regard to only one of the analytical sections, but not of the process as a whole.

As experience shows, in order to assure the accuracy of results of quantitative analysis block (elemental) verification is not quite sufficient. A way out, found in practice, is that besides such verification, the accuracy of the final result of analysis is monitored on the basis of rather a cybernetic approach, when, more or less disregarding the internal processes in the system, a study is undertaken of the relation between the input and output parameters. In metrological terminology, this method is closer to that known as an overall (thorough) verification, although its possibilities are much wider than the traditional ones: it enables the analyst to assure the control of accuracy of analytical results quickly and directly at the operation site, with such a time schedule which is necessary in line with the conditions of the task.

Of the means employed for such a verification, the most effective are the reference materials. In this usage, there is reason to attribute to the latter the term reference materials for overall (thorough) verification (or "overall calibration", if they are employed for this purpose). As shown in Figure 11, the use of such materials is indicated by a horizontal arrow passing through all the stages of the process (shown as example is the first level). In contrast to the reference materials used for the block verification (or calibration), such materials employed for overall checking (or calibration) should be differentiated, taking into account the composition of the materials being analyzed and often the peculiarities of the analytical methods.

Important from the methodological point of view is the subdivision of the reference materials into the two principal groups.

The use of other means (e.g., the standard additions method) usually also can be defined as a variant of the overall verification, although their employment for block verification is not excluded.

If the diagram, shown in Figure 11, from the structural point of view degenerates into one with a single element, i.e., containing only one section at a certain level, then the functions of reference materials, in both the block and overall verification methods (calibration), for this level coincide.

The relationship indicated by the vertical and horizontal arrows in Figure 11 essentially express the notion, which in the reports[164,165] is called traceability.

2. *Variants of Reproduction and Transmission of Measurement Information onto the Level of Field Analyses*

In the course of reproduction and transmission of measurement information for the purpose of the block verification (calibration) schemes are realized which are typical for the widely accepted metrological practice.[3,22,50] Their common feature is the multiplicity of stages and certification of the definitive means (upper tier) in one single laboratory, through the use of a single, specially developed or improved method. This applies to linking not only with the classical verification schemes (e.g., for measurements of mass), but also with the newly adopted schemes, often including reference materials (e.g., for gas-analytical measurements[166,180]). The elimination of errors (systematic), is ensured by refining of the definitive means and also by periodic comparison in the course of regular service.

Regarding the reproduction and transmission of information for the purpose of overall verification, in this case a number of techniques (see Section III.B.) are realized, the most effective of them all, as noted above, being the use of reference materials. They have the rank of RMs (i.e., legitimized means of measurement) or materials having an application sphere not duly legitimized.

Refer to Figure 12 for the general diagram of practical applicable variants of reproduction and transmission of measurement information on the contents. The lower block in this schematic diagram depicts the field analyses which compare with the basic block shown in Figure 11. The transmission of measurement information is shown by arrows: continuous arrows — information on contents; dashed arrows — information on intermediate magnitudes (mass of sample or precipitate, solution volume, light-absorption data, electric conductivity, etc.). If the above links are viewed in reverse direction, then this corresponds to the traceability concept.

Considering the above-mentioned scheme it is to be noted that: (1) besides the definitive and reference methods, there exist and are widely used for development of RMs "suitable" methods which have better metrological characteristics, as compared with the field methods (e.g., when producing RMs on the basis of the "round-robin" analysis); (2) besides the definitive, reference and the suitable methods of analyses, there is the possibility of realizing the respective methods as techniques for synthesis of substances having a predetermined chemical composition (e.g., the methods of producing RMs, such as mixtures of gases, pure oxides, etc.). Of course the term synthesis in connection with such a procedure will be differing from the definition accepted, for example, in organic chemistry); (3) in a definite situation only one, as a rule, of the possible variants of transmission of measurement information onto the level field analyses is realized, which is due to the expediency and also to possibilities and the limitations of the analytical service; in case of the chemical analyses more often this realization is achieved by transmitting the data along the following chain: suitable method (methods) → primary (secondary, tertiary) RMs → field methods; (4) quite often instead of three categories of RMs only two, or even one, will be sufficient; (5) the classical metrological means (upper block in Figure 12) are intended for the purpose of performing operations with the use of instrumentation in the course of analysis and also for the block verification and calibration.

It is hoped that the diagrams presented in Figures 11 and 12 and the principles on which they are based will promote a better understanding of the relationship between RMs and other substances and materials of similar application, on the one hand, and the system of basic measurement units, on the other.

3. Relevant Factors, Projects and Experience Gained in Solving the Problem

a. Number of Particular Schemes and Their Optimization

The vast majority of analytical methods require a relatively high differentiation in regard to the composition of the substances being analyzed. The great diversity of combinations of components making up the basis of various substances and contained in the form of impurities, as well as the wide ranges of their contents, force the analytical service to use many thousands of modifications of methods of quantative analysis of inorganic and organic substances at the level of field analyses (measurements). As a result of this, the number of types of RMs in current use attains several thousand, while the demand for them is apparently an order higher. The number of methods used for monitoring the results of field analyses and for other precision determinations, although somewhat smaller, is still considerable. As a consequence of this, the number of indivudal subsystems employed for the reproduction and transfer of measurement information on the chemical composition attains a magnitude of the order mentioned above. Hence, the great difficulties encountered in scientific and organizational work associated with the creation of a metrologically effective analytical service. It is apparent that there exists a necessity of formulating a principle of optimization of the number of individual subsystems. Utilizing the same approach employed for the optimization of RM subsystems and calibration characteristics (see Section IV.B.), the

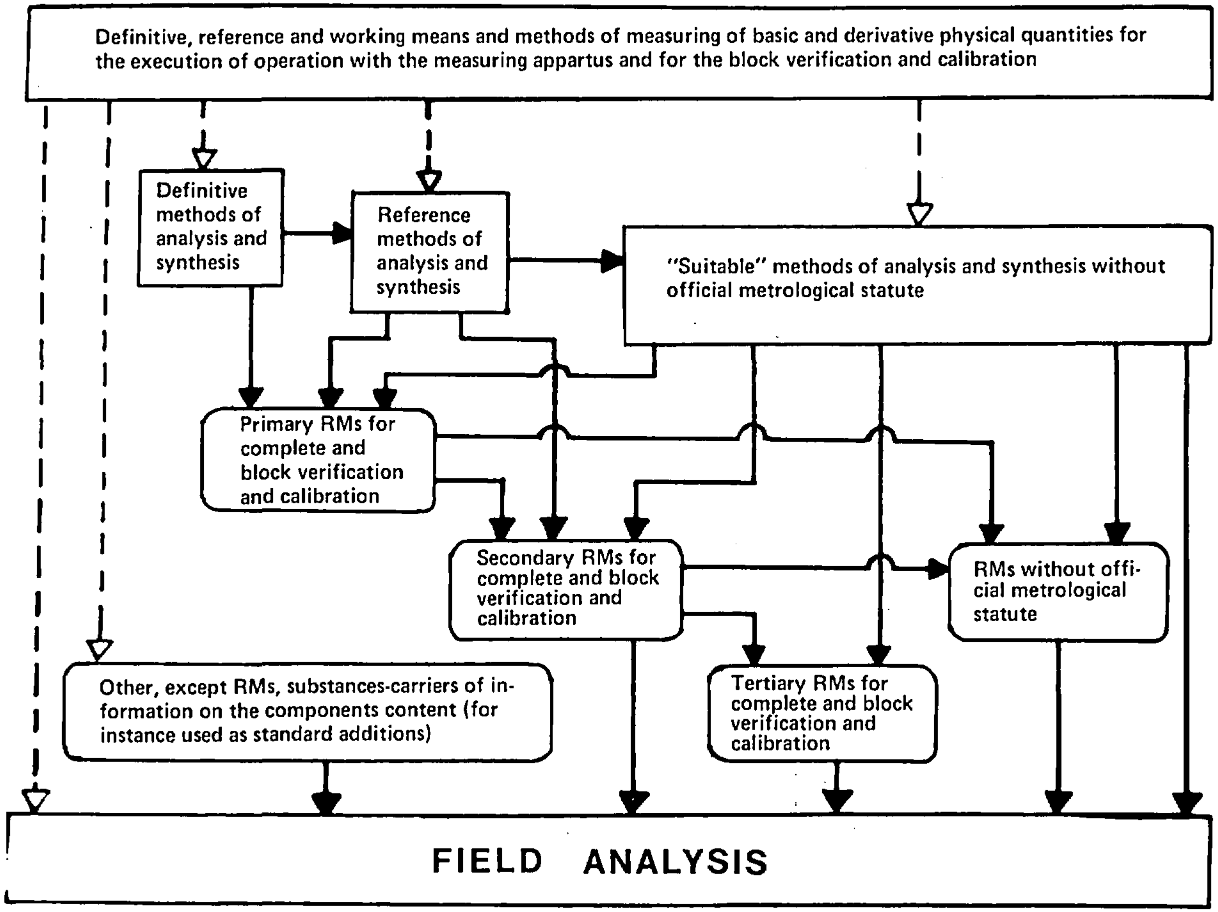

FIGURE 12. General diagram of used variants of reproduction and transfer of measured data on the content of components in substances.

following definition has been suggested:[169] "the optimum number of hierarchical chains of transfer of measurement information is one that ensures a given accuracy of results of field analyses of a maximum number of substances with the aid of a minimum number of particular chains".

Among the factors determining the optimum number of such hierarchical chains, the following have been mentioned and examined:[169] the number of specific variants of field analysis methods, the number of RM types (this depending not only on the number of specific variants of field analysis methods, but also on the range of contents of components) and, finally, the number of specific variants of definitive and comparative methods combining reliability and universality. The latter property is enhanced as we pass from methods based on chemical reactions (interaction, mainly of valence electrons) to methods based on the transition of inner orbit electrons (X-ray spectral analysis) and especially to methods based on nuclear reactions.

It is important to use well established criteria for tolerable values of field analysis errors, which may arise, if several analyzed substances (groups of substances) are jointly served by a common hierarchical chain.

b. Projects and Experience Gained in Solving the Problem

The following scheme was proposed in 1949 for inorganic substances of complex composition.[40] For each element there must be provided a main standard substance, the level of purity of which must be established with a requisite accuracy. This substance should be easily reproducible and stable in time. On the basis of this substance a primary standard solution is to be prepared with a reliably established concentration of the element being certified. Composite standard solutions are to be prepared from the primary standard solutions by mixing together exactly measured quantities of the latter. The composite standard solutions are to serve as models of the substances (to a good approximation) obtained by bringing the analyzed RMs into the solution. Composite standard solutions were intended to perform the functions of primary RMs. Under this scheme the certification was to be carried out in one laboratory as a thoroughly planned and executed experiment. The implementation of such a scheme aimed at the certification of RMs for spectrochemical analysis of steels using optical emission methods and composite standard solutions has been described elsewhere.[140]

In 1950 to 1953 a metrologically well founded technique of synthesizing RMs to be used for calibration purposes in spectrochemical analysis of metals transformed into oxides, was suggested and implemented.[181] An alleviating feature of this technique is that it is insensitive to the nonconformity between the forms of compounds of elements in the RMs and in the analyzed specimens (globular arc method). This circumstance has made it possible to produce a chain with a minimum number of sections: (1) RMs synthesized from oxide mixtures; (2) their use for calibration in field analyses.

Proposals on the structure of a hierarchical chain for the verification of analytical instruments were published in 1963.[166] The top tier included a definitive method of determination of concentrations (coulonometric) or, in the more general case, reference means for measurement of the fundamental quantities: mass, volume, pressure, resistance, etc. These suggestions are being implemented in the field of development of hierarchical chains for the verificaion of gas analyzers, pH-meters, and moisture indicators.

Suggestions on the establishment of a system for the measurement of chemical composition based on substances used for transferring the value of the mole were published in 1975.[17] Their gist is not very different from that of methods based on the measurement of the ratio of mass of the component being determined to that of the whole sample with all the ensuing specific circumstances (see Sections I.B. and VI.B.1.).

Recommendations made in the preceding papers, as well as the comparison method developed for the certification of RMs,[2,167,168] have been used in the working out of a generalized hierarchical chain and in substantiating the feasibility of its implementation with the provision of a required margin of accuracy at different levels.[169]

The top level in such a hierarchical chain is a set of definitive (standard) substances of sufficiently high purity. Modern metallurgical and chemical technology provides relevant high-purity products; there are even substances having high isotopic purity.

From the primary substances it will be possible by metrologically correct synthesis to prepare substances having the rank of special standards of chemical composition, modeling with a maximum degree the composition and other analytically important properties of substances (materials), from which the subordinate reference means — primary RMs — are to be made. A good stock of primary substances will provide for the modeling of various combinations of elements (compounds). The special standards must be, with a few exceptions (composition of gas mixtures, for example), synthesized not immediately before use, but beforehand, on the basis of a thoroughly planned and executed metrological experiment. The main purpose of special standards is to provide a means for the storage, reproduction, and transfer of values of the units of quantities characterizing the contents of components in substances and materials.

The next level is that of the primary RMs (as to their purpose, see below). The transfer of measurement information from a special standard to a primary RM may take place in several ways depending on the practical expediency. If the primary RM is made by synthesis (for example, from oxides of elements or from pure gases, liquids), then the special standards can be used for monitoring the accuracy of synthesis of such a substance: the latter may for this purpose be compared with the standard (for instance, by the pair comparison method[2,167,168]). If such a substance has been produced from "natural" materials (ores, alloys, etc.) and must therefore be analyzed, the measurement information stored in the special standard may be used for monitoring the accuracy of the results of certification analyses or for the direct transfer, if the composition of the primary reference material is established by comparison.

The main purposes of primary RMs are monitoring the accuracy of results in the course of development and utilization of reference and similar in importance methods of analysis; direct transfer of measurement information to the next levels—those of the secondary and tertiary RMs by the comparison method. The main purpose of secondary RMs is monitoring the accuracy of results obtained by working methods employed in field analyses, etc. Tertiary RMs are intended for the same purpose as the secondary RMs (if the category of tertiary substances is justified).

A demand arises for special standards whenever it is found more difficult to prepare RMs with sufficiently low errors of certified contents than it is to compare them with substances having the rank of a special standard. When no such necessity exists, the hierarchical chain is simplified correspondingly. It is also simplified when two, and not three, categories (primary, secondary) or even one, performing the functions of three, are sufficient. In the latter case, if it is called for, an alternative is possible: a special standard — RM of one category. Finally, we can limit ourselves to the chain: (1) primary, (2) secondary (tertiary, if necessary) RM. Thus, this chain is sufficiently versatile; many of the schemes in current use are individual cases of this chain. Its special feature is the more widely practiced transfer of measurement information by means of comparison with a means having higher metrological characteristics, which in many cases gives the greatest efficiency. In individual cases it may serve as a chain for unit-by-unit verification (calibration).

The fact that primary substances and special standards are expended in the considered cases (just as primary RMs) is no obstacle: it is possible to restore the original stock by comparison of the initial and newly supplied substances. For this purpose the most economical is the comparative method.[2,4,6,167,168,170]

Systems utilizing primary and other RMs are, of course, no novelty. Often it is assumed that it is sufficient to have a primary RM more reliable than the secondary. In contrast to such a metrologically imprecise principle, the hierarchical chain[169] and others similar to it, applied in the field of ferrous metallurgy products,[4,6,168,170,182] provide a more stringent approach. First, the requisite reliability of field analyses underlies the initial reasoning. Second, with this in view, two important characteristics are planned, ensured, and proved: a sufficient margin of reliability for RMs used directly for monitoring field analyses, and a sufficient margin of reliability for RMs of higher rank, as compared to the ones used.

Note that actual situations prove to be more complex than those envisaged in schemes: it is possible that at the initial stages a margin of reliability cannot be ensured even for those RMs which are intended for the direct monitoring of the accuracy of field analyses (or calibration). Such situations often occur, for example, when RMs of rather complex composition are first issued. On the other hand, the use of such imperfect RMs is a step toward the improvement of the accuracy of results of field analyses or the calibration system. In such cases it is apparent that all-or-nothing is not a good precept to follow. It is important to be aware of the quality level of such RMs and have this in mind when using them.

C. Systems Approach — Basis for Further Development

The great amount and importance of data on the chemical composition and structure of substances, the large human and material resources expended for obtaining such information, as well as the complexity of the tasks undertaken make the solution of the problem of optimization of the activity of the analytical service very urgent. This problem can be most effectively solved through recourse to the systems approach. Several roads are visible in the working out of such an approach in this field. They do not contradict, but complement one another, being related to different aspects and levels of generality. Thus, we note the description of the analytical process by means of terms and notions used in the systems theory,[183-185] the listing and main functions of the components of a measurement system,[3,22,122,186,187] systems analysis of RM function in the physicochemical measurement process,[188] etc. At the same time it is important to stress that for the most effective solution of the problem, it is insufficient to employ corresponding terms and notions, classifications, to indicate the main subsystems and the connections between them.

In general a typical systems approach program includes: determination of the object under consideration; formulation of the general idea of the system with due regard for the aims of the top level systems; requirements to be met for the attainment of the general aim; working out of criteria for deciding whether the requirements are met fully; establishment of the structure of the investigated system, determination of its limits, and external links; specification of tasks for each part of the system and individual criteria for the assessment of its performance, building a functional model of the system for the purpose of investigating its possibilities, limitations, and variants; making decisions on optimization and their implementation.

These considerations make it necessary to regard the activity of the analytical service and of the subsystems catering to it (for instance, the subsystem responsible for providing RMs) not separately, but in conjunction with the aims of the upper tier systems (production and consumption, protection of the environment, health care, etc.) and the links with adjacent systems, for example, standardization of materials and testing methods. In principle, such an approach is implemented more or less fully almost always. But it is important to make the next step: ensure the possibility of carrying out of substantiated calculations with the aim of optimizing the activity of not only the analytical service, but of all the associated systems from the point of view of the objectivity of conclusions on the quality of materials, state of technological processes, protection of the environment or human health.

The expenses — wastes[114-121] principle is a known approach to optimization. For the implementation of this principle it is necessary to fulfill several conditions. First of all, one should know the sum of expenditures (this usually does not entail any difficulties). Then, one should know what part of the objects (for instance, batches of chemical products) is assessed incorrectly (for example, down-graded) or what is the probability of a poor assessment of the quality of a separate batch of a product, the state of a separate environment region, etc. This involves taking into account the probability of errors of the first and second kind, as the statisticians say. Finally, one should know what are the economic consequences of erroneous conclusions in each specific situation. Such data are usually unavailable and cannot be assessed directly.[3] Besides, the losses due to the imperfections of a system may be not only of economic nature, but also ecological, for instance. Some of the consequences of analytical results having an insufficient reliability have been reviewed above (see Section II.C.8.).

With due regard for the noted difficulties and limitations, a theory and calculation techniques have been developed for the solution of the problem on the basis of a different optimization criterion: agreement (closeness) of values of characteristics describing the required and attainable reliability.[2,7,16,25,30,44-47,91-93,117] The realization of such an approach has also been reviewed elsewhere.[6,13,14,21,23,48,49,189] A comprehensive treatment of the activities of the analytical service as a large system and of the systems associated with it is given elsewhere.[2,6-8,13,16,21,25,30,45-47,190,191]

It has been recognized that the considered problem is a complex one[2,7,25] and its successful solution depends on the concerted action of analysts, metrologists, and standardizers. A summary of the main tasks to be undertaken using the systems approach is given elsewhere.[2,7,25,92] These include:

1. Establishment (substantiation) of the requirements of production and consumption, protection of the environment, health care, as well as scientific research into the reliability of results of each variety of quantitative analyses.
2. Estimation of the actual level of reliability of such results, comparison with requirements, detection of weak spots.
3. Concordance between requirements and possibilities of the analytical service (in the first place, with application to weak spots): improvement of methods, instrumentation, development, and use of RMs and other means of similar purpose; introduction of systems for the statistical control of the reliability of analytical results; comprehensive (metrologically approved) standardization of materials and their testing methods (including analyses), certification of nonstandardized methods, accreditation of laboratories, on the one hand, and a critical evaluation of requirements, on the other.

Each of these comprises, of course, many individual problems.

The most important general conclusion to be made[2] is that there is a growing need for the establishment of a metrologically effective system of quantative analyses (measurements) of the chemical composition of substances, similar to those organized for other kinds of measurements.

The difficulties encountered on the way to solving this problem are apparently greater than those met earlier in other fields of measurement. However, the significance of the problem justifies the expenditure of effort.

It seems that such an approach should be implemented also in application to the measurement of physicochemical and other properties of substances.

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